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## X-ray diffraction studies of rare-earth metaphosphate glasses

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**Abstract.** X-ray diffraction measurements have been performed at the Synchrotron Radiation Source, Daresbury, UK, in a structural study of the rare-earth metaphosphate glasses  $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.794}$ ,  $(\text{Eu}_2\text{O}_3)_{0.252}(\text{P}_2\text{O}_5)_{0.748}$  and  $(\text{Tb}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$ , whose compositions were determined by electron microprobe analysis. Such rare-earth metaphosphate glasses  $\text{R}(\text{PO}_3)_3$  containing high concentrations of rare-earth  $\text{R}^{3+}$  ions are of growing interest in fundamental studies of magnetic glasses and in optical communications and laser technologies. The diffraction results prove to be consistent with a network model which is dominated by a phosphate glass skeleton having three-dimensional connectivity, constructed from  $\text{PO}_4$  tetrahedra linked to adjacent tetrahedra via bridging oxygen atoms. Results relating to rare-earth–oxygen correlations are consistent with a sixfold to eightfold coordination of the rare-earth atoms, with distances showing the trends expected from the lanthanide contraction: a reduction of the rare-earth ionic radii with increasing atomic number.

### 1. Introduction

There is much interest in the rare-earth metaphosphate glasses  $(\text{R}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$  (where R represents one of the rare-earth elements) both as vehicles for testing the general applicability of recent theoretical models introduced to account for the dynamics of amorphous materials, such as the soft potential [1–5] and phonon–fracton [4, 6] models, and also because of their potential applications in laser and optoelectronics technology [7–10]. In these glasses the rare-earth ions are incorporated into the matrix in very large modifier concentrations, rather than at the low dopant levels usually employed in devices, so they show highly novel magnetic and magneto-optical properties [11]. The metaphosphate  $\text{R}(\text{PO}_3)_3$  is a particularly stable composition and such glasses are also unusually water stable, a particularly valuable feature for device applications. To improve the general understanding of the wide range of properties that these glasses possess, a series of experiments of which the current study is a part were undertaken to probe their atomic-scale structure. Indirect structural information was first obtained from the Raman spectra which showed that the vibrational modes are consistent with the network skeleton being comprised of linked  $\text{PO}_4$  tetrahedra [12, 3]. A recent direct structural study [16], employing the complementary probes EXAFS and

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x-ray diffraction, has established that the terbium metaphosphate glass of composition  $(\text{Tb}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$  does have a network built up from  $\text{PO}_4$  tetrahedral units, most pairs of  $\text{PO}_4$  sharing one corner. Since the rare-earth metaphosphate glasses show a wide variety of physical properties, which vary markedly from one rare-earth modifier to another, it is necessary to find out whether there are any pronounced structural differences from one series member to another. A comparative EXAFS structural study carried out on a range of rare-earth metaphosphate  $\text{R}(\text{PO}_3)_3$  glasses modified with Pr, Nd, Eu, Gd, Tb and Ho, using their respective rare-earth  $L_{\text{III}}$  absorption edges [13], provided information on the local environment of the rare-earth ion within the phosphate glass matrix. The rare-earth ions were found to occupy sites with an average coordination number in the range  $6 \leq N \leq 8$ , the surrounding atoms being oxygen. Evidence was obtained for a rare-earth–phosphorus correlation distance of between 2.7 Å and 3.6 Å, and a further rare-earth–oxygen correlation at approximately 4 Å. The EXAFS spectrum showed no evidence for R–R correlations within the short-range order, a result especially pertinent to the optical and magnetic properties of the glasses. The fractal bond connectivity  $4C_{11}/B$  [14, 15] of these glasses, obtained from the elastic stiffnesses determined from ultrasonic wave velocities, was found to range between 2.3 and 2.8, indicating that their connectivity tends towards having a three-dimensional character.

X-ray diffraction studies have now been made to characterize the short-range structure of metaphosphate glasses modified with Pr and Eu; for completeness the results are compared with those previously presented on the terbium metaphosphate glass [16].

**Table 1.** The series of metaphosphate glass samples.

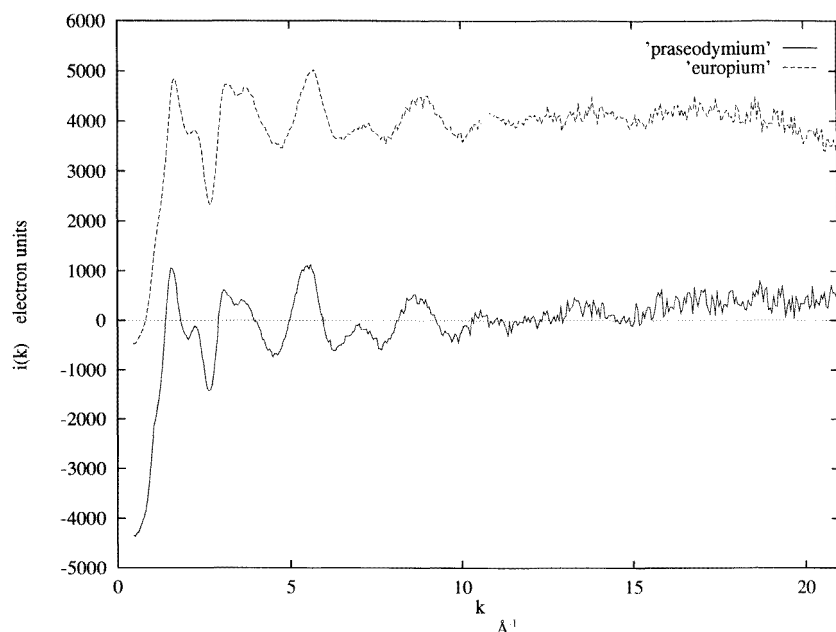
Metaphosphate glass	Composition
Praseodymium	$(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.794}$
Europium	$(\text{Eu}_2\text{O}_3)_{0.252}(\text{P}_2\text{O}_5)_{0.748}$
Terbium [16]	$(\text{Tb}_2\text{O}_3)_{0.26}(\text{P}_2\text{O}_5)_{0.74}$

## 2. Experimental procedure

The glass was prepared as described by Mierzejewski *et al* [12]. High-purity dry rare-earth oxide and  $\text{P}_2\text{O}_5$  were mixed in pre-weighed proportions in alumina crucibles, placed in an electrical furnace and heated to approximately 1500 °C. The resultant melt was poured into a steel mould preheated to 500 °C, annealed and then cooled slowly. The compositions of the glasses were determined by electron probe microanalysis, using single crystals of  $\text{PrP}_5\text{O}_{14}$  and  $\text{EuS}$  as standards. These glasses form in the stable metaphosphate composition range, nominally 25% rare-earth oxide. The final constituent ratios for the glasses studied here are given in table 1. To avoid any possible contamination with water, the glasses were stored in a desiccator. The water content of the glasses was less than 0.1 mol%, as measured by a fast Fourier infrared absorption technique. Although most phosphate glasses are typically extremely susceptible to water contamination, these metaphosphate glasses are not. This increased chemical durability is probably due to the increased polymerization of the glass network induced by the high-valence rare-earth ions, whose presence promotes increased cross linkage between corner-sharing  $\text{PO}_4$  tetrahedra making up the bulk of the glass [16–19]. The glass samples used for the diffraction experiments were powdered, first by crushing between two steel plates and then in a mortar and pestle; the resulting fine glass powder

could then be dusted in a thin layer onto tape for mounting in the x-ray beam. It was important to keep the powder layer reasonably thin as the x-ray absorption properties of these glasses are particularly severe.

The experiments were performed at the SRS, Daresbury, UK, on station 9.1. Beamline 9 receives synchrotron radiation from a 5 T superconducting wiggler magnet which provides the high intensity at short wavelengths necessary to measure diffracted intensity to high  $k$ -values ( $k = (4\pi \sin \theta)/\lambda$ ). The diffraction experiment was performed in a conventional theta/two-theta ( $\theta/2\theta$ ) transmission geometry and at an x-ray wavelength of 0.5 Å. The  $\theta/2\theta$  geometry was chosen as it simplifies many of the necessary corrections. The  $2\theta$  angular range over which diffraction data were collected was  $2^\circ$  to  $130^\circ$  in  $0.2^\circ$  steps giving a  $k$ -range of 0.4 to  $23 \text{ \AA}^{-1}$  (although it was not possible to attain this full range in practice due to difficulties encountered in fitting the self-scattering contribution, a more realistic estimate of the usable  $k$ -range being 0.4 to  $21 \text{ \AA}^{-1}$ ).

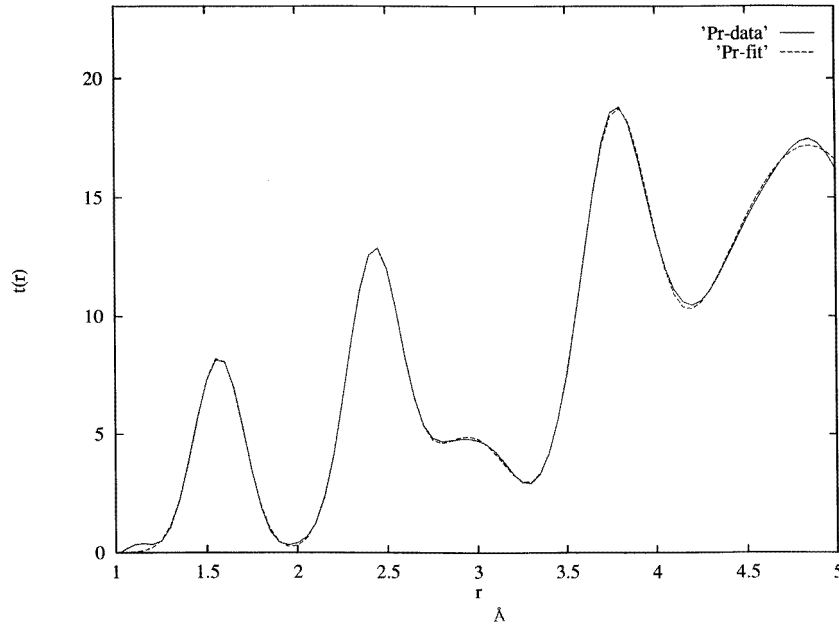


**Figure 1.** The interference function  $i(k)$  obtained for praseodymium metaphosphate glass (solid line) and for europium metaphosphate glass (broken line and axis shifted from zero for clarity).

### 3. Diffraction data analysis

The diffraction data have been corrected for beam polarization, variations in incident flux, background scattering effects, and sample illuminated volume variation with rotation and absorption, following correction procedures described by Huxley [20]; general data analysis is based upon the text by Warren [21]. The structure factor (or interference function)  $i(k)$ , using Warren's notation, is obtained by the relationship

$$i(k) = \left( \frac{I_{eu}}{N} - \sum_{uc} f_j^2 \right) / f_e^2 \quad (1)$$



**Figure 2.** The electron density distribution function  $t(r)$  for the praseodymium metaphosphate glass. The experimental data are given by the solid line and a five-gaussian fit by the broken line.

where  $I_{eu}$  is the corrected intensity function,  $N$  is the number of scattering units ('units of composition', uc) in the sample, scaled to unity,  $f_j$  is the atomic self-scattering function for atom type  $j$  within the unit of composition and  $f_e$  is an average electron scattering form factor evaluated from a knowledge of the total number of electrons in the defined unit of composition and the calculated total atomic scattering factor. The electron density distribution function  $t(r)$  was evaluated using the Fourier transform relation

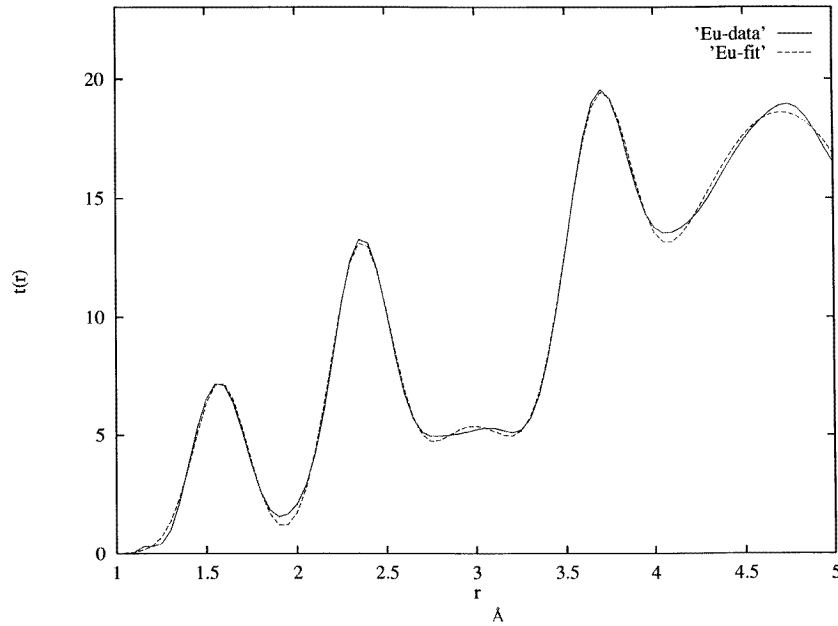
$$t(r) = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_{k_{\min}}^{k_{\max}} ki(k)w(k) \sin(kr) dk \quad (2)$$

where  $\rho_e$  is the average electron density of the sample and  $\sum_{uc} Z_j$  is the total number of electrons in the scattering unit;  $w(k)$  is an applied window function for suppressing Fourier transform ripples [22]. For this particular analysis, the function applied was

$$w(k) = \begin{cases} 1 - 3(k/k_{\max})^2 & |k| < k_{\max}/3 \\ \frac{3}{2} \left( 1 - 2|k/k_{\max}| + (k/k_{\max})^2 \right) & k_{\max}/3 < |k| < k_{\max} \\ 0 & |k| > k_{\max}. \end{cases} \quad (3)$$

This electron density function  $t(r)$  is weighted in electrons and is fitted with pair functions defined by

$$P_{ij}(r) = \int_0^{k_{\max}} \frac{f_j f_i}{f_e^2} w(k) \sin(kr_{ij}) \sin(kr) dk \quad (4)$$



**Figure 3.** The electron density distribution function  $t(r)$  for the europium metaphosphate glass. The experimental data are given by the solid line and a five-gaussian fit by the broken line.

where

$$t(r) = \sum_{uc} \sum_i \frac{N_{ij}}{r_{ij}} P_{ij}(r). \quad (5)$$

Data analysis proceeds by calculation of the  $P_{ij}$  for various  $r_{ij}$  with known atom type pairings, such as P–O and Pr–O, assigned to distances that correspond to peak positions within the  $t(r)$  curve. The area of the pair function is then scaled to the area of the peaks in the  $t(r)$  curve, the scaling factor being the coordination number  $N_{ij}$  (corresponding to the number of atom pairs at distances  $r_{ij}$  in the scattering unit of composition). Due to the complex nature of the composite distribution function  $t(r)$  obtained from a single diffraction experiment, independent information (such as from EXAFS) helps in the process of extracting physically meaningful information from the data.  $t(r)$  is a function representing the electron density variations within the system, and is therefore difficult to interpret in a simple manner. If the first few peaks in the function at low  $r$  are independent, it is possible to make a reasonable estimate of coordination numbers; however if they are not isolated features, this becomes more difficult, or even impossible. The criterion that  $t(r)$  be zero below the first physically acceptable atomic correlation distance is not valid in the case of x-ray studies, since it is the electron distribution that is being probed.

Unfortunately, due to the nature of phosphate glasses, absolute determination of a suitable scattering unit from which to scale the diffraction data is problematic, due to the  $P_2O_5$  volatilization losses during the manufacture of the glass. Accordingly, and in line with the microprobe results mentioned above, constituent ratios for a suitable base unit of composition have been chosen to correspond to the metaphosphate glass stoichiometry of  $R(PO_3)_3$  close to the actual compositions (table 1). The problem of unknown component ratios is common when dealing with doped phosphate glass systems,

and this has a detrimental effect on the accuracy of the theoretical determination of the atomic self-scattering function,  $\sum_{uc} f_j^2$ . The difficulty is further compounded by uncertainties in determining exact incoherent scattering contributions and absorption losses, and leads necessarily to an increased uncertainty in the estimation of the corrections that need to be applied to the data.

#### 4. Results and structural information

The functions  $i(k)$  and  $t(r)$  derived from the diffraction data for the praseodymium and europium metaphosphates are shown in figures 1–3, whilst those for the terbium analogue may be found in Bowron *et al* [16]. A cursory analysis shows that the positions of the first main feature in the functions  $t(r)$  are consistent with the bulk phosphate glass network (table 2); the second peak in the functions  $t(r)$  contains contributions from both the rare-earth–oxygen and oxygen–oxygen correlations present in the glass, although the rare-earth–oxygen correlation dominates due to the number of electrons associated with the rare-earth atom. The peak positions were determined by fitting a series of gaussians to the data.

**Table 2.** X-ray diffraction results.

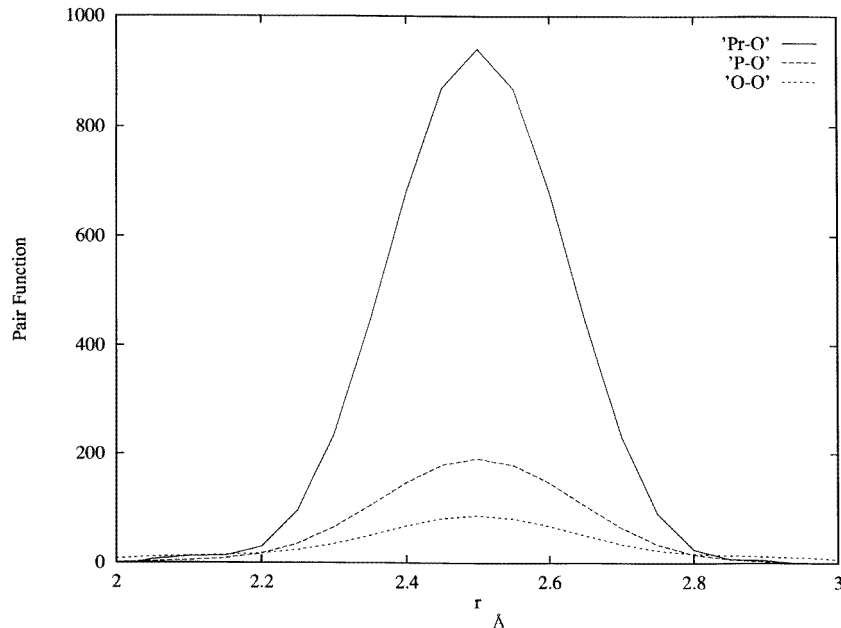
Sample	Peak position (Å)	Peak area of fitted Gaussian profile ( $\propto$ electrons <sup>2</sup> )	Atomic correlation(s) assigned
(Pr <sub>2</sub> O <sub>3</sub> ) <sub>0.216</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.794</sub>	1.57 ± 0.05	2816	P–O
	2.43 ± 0.05	4762	Pr–O and O–O
(Eu <sub>2</sub> O <sub>3</sub> ) <sub>0.252</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.748</sub>	1.58 ± 0.05	2770	P–O
	2.36 ± 0.05	5640	Eu–O and O–O
(Tb <sub>2</sub> O <sub>3</sub> ) <sub>0.26</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.74</sub> [16]	1.58 ± 0.05	2483	P–O
	2.34 ± 0.05	6245	Tb–O and O–O

**Table 3.** Pair functions  $P_{ij}$ .

Sample	Pair function	Interatomic separation (Å)	Area ( $\propto$ electrons <sup>2</sup> )
(Pr <sub>2</sub> O <sub>3</sub> ) <sub>0.216</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.794</sub>	P–O	1.60	105
	Pr–O	2.35	447
	O–O	2.50	30
(Eu <sub>2</sub> O <sub>3</sub> ) <sub>0.252</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.748</sub>	P–O	1.60	104
	Eu–O	2.30	330
	O–O	2.50	30
(Tb <sub>2</sub> O <sub>3</sub> ) <sub>0.26</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>0.74</sub> [16]	P–O	1.60	103
	Tb–O	2.30	340
	O–O	2.50	30

The first peak at 1.57 Å is characteristic of the P–O correlation expected for any phosphate glass system consisting of linked PO<sub>4</sub> tetrahedra; for example the P–O distance has been measured as 1.55 Å [23] and 1.6 Å [24]. The O–O distance has been determined to be 2.50 Å [23] in previous studies of metal-doped phosphate glasses, but in the present case, due to the similarity between the distance associated with the rare-earth–oxygen and

oxygen–oxygen correlations, individual assignments cannot be made. The average second correlation distance, i.e. that involving rare-earth–oxygen correlations, displays a trend that is consistent with the lanthanide contraction: the reduction in size of the rare-earth ion as the periodic table is traversed. Several other peaks are visible in the  $t(r)$  curves, but a definitive assignment of atomic correlations becomes impossible beyond the second peak.

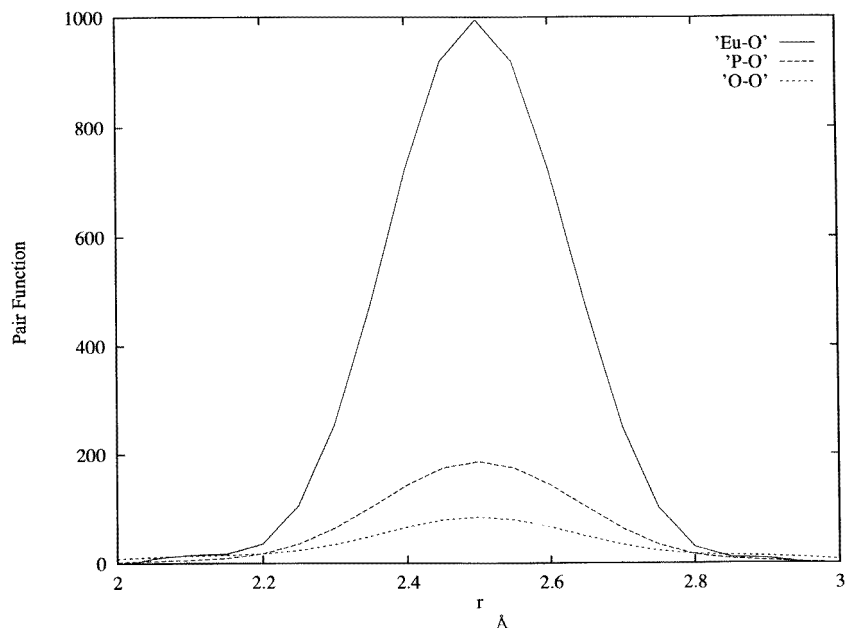


**Figure 4.** Interatomic pair functions calculated for the praseodymium glass: Pr–O, P–O and O–O, evaluated at an interatomic distance of 2.5 Å.

The areas of the first two peaks have been evaluated from the fit, and calculated pair correlation functions  $P_{ij}$ , shown in figures 4 and 5, are summarized in table 3. These have been derived for the P–O, R–O and O–O combinations. The magnitudes of these pair correlation functions show the dominance of the rare-earth-ion contribution to the x-ray diffraction pattern; regions of  $t(r)$  where the contributions from these metal ions are significant are difficult if not impossible to interpret in terms of any other atomic network contributions. Care must be taken when interpreting the peak areas of these functions in the course of extracting coordination number information, since a large part of an area may be contained in the wings of the transform function used to determine the  $P_{ij}$ . The errors associated with the peak areas in the  $t(r)$  functions are also large, due to difficulties in assigning a unique set of weightings to the series of gaussian profiles that are used to fit the peaks. This problem with the gaussian profile weightings is largely due to the features not being totally isolated in the composite radial distribution function accessed via the x-ray diffraction technique, and allowance must be made for this overlap when determining approximate values for coordination numbers. With consideration of these two problems, an estimate of the total variation which can result in the coordination numbers extracted using a simple model interpretation of the pair distribution functions is  $\pm 25\%$ .

The peak positions in the  $t(r)$  are evaluated to within  $\pm 0.05$  Å, and are more robust than the associated coordination numbers. Due to the large uncertainty in the areas, coordination





**Figure 5.** Interatomic pair functions calculated for the europium glass: Eu-O, P-O and O-O, evaluated at an interatomic distance of 2.5 Å.

values are only useful semi-quantitatively as a guide to structural parameters; here for example it was possible to test whether the magnitude of the areas of the first two peaks would be consistent with P-O and R-O/O-O correlations predicted by a simple model approximation (an example calculation for silica is given in [25]). To model the first feature in the  $t(r)$  function, we assumed a base structural model of three phosphorus atoms in the scattering unit, each bonded to four oxygen atoms; this model proved to be consistent with the experimental results. The area of the second peak, assuming the correlation to be dominated by terms involving the rare-earth species R (R-O and O-R), is indicative of the relatively high coordination of these metal ions; values ranging between five and nine nearest oxygen neighbours are found, and this result is consistent with EXAFS data obtained for a number of rare-earth metaphosphate glasses [13]. A summary of the oxygen coordination number for phosphorus and the rare-earth species in each of the glasses is given in table 4.

## 5. Discussion of the structure of the rare-earth metaphosphate glasses

The structure of these metaphosphate glasses is based on a polymeric network of PO<sub>4</sub> tetrahedra linked via bridging oxygen atoms, the trivalent rare-earth ions occupying sites inside the skeleton of PO<sub>4</sub> units.

The study of a terbium metaphosphate (Tb<sub>2</sub>O<sub>3</sub>)<sub>0.26</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>0.74</sub> glass [16] using the combination of x-ray diffraction and EXAFS techniques established that rare-earth metaphosphate glass is built up from PO<sub>4</sub> tetrahedral units, most likely with pairs of PO<sub>4</sub> tetrahedra sharing only one corner. The present observation that the first x-ray diffraction peak (table 2) occurs in the range 1.55 Å to 1.60 Å characteristic of the P-

O correlation for a phosphate glass indicates that the structures of  $(\text{Eu}_2\text{O}_3)_{0.252}(\text{P}_2\text{O}_5)_{0.748}$  and  $(\text{Pr}_2\text{O}_3)_{0.216}(\text{P}_2\text{O}_5)_{0.794}$  glasses also comprise linked  $\text{PO}_4$  tetrahedra. In general, chains, rings and branched polymeric units of interconnected  $\text{PO}_4$  tetrahedra can be produced by sharing oxygen atoms between the tetrahedra [9]. In vitreous  $\text{P}_2\text{O}_5$  each  $\text{P}^{5+}$  ion is bonded to three bridging (POP) oxygen atoms with bond values of 1.0 valence units, and one terminating oxygen with 2.0 valence units [18, 19, 26].

**Table 4.** Approximate evaluation of coordination numbers in each glass.

Sample	Peak position ( $\text{\AA}$ ) ( $\pm 0.05 \text{\AA}$ )	Approximate coordination number of oxygen atoms ( $\pm 25\%$ )
Pr	1.57	4.4 about P
	2.43	5.3 about Pr
Eu	1.58	4.4 about P
	2.36	8.5 about Eu
Tb [16]	1.58	4.0 about P
	2.34	9.2 about Tb

The  $Q^n$  notation [26], where  $n$  is the number of non-bridging oxygens per tetrahedron, is useful for discussing the format of the tetrahedra. The  $\text{P}_2\text{O}_5$  glass structure is based on  $Q^3$  tetrahedra. Three types of building unit are available from which a phosphate glass skeleton can be constructed: (i) the branching tetrahedron in which three oxygen atoms are shared with neighbouring  $\text{PO}_4$  units; (ii) the middle tetrahedron in which two oxygen atoms are shared with neighbouring  $\text{PO}_4$ , and there is one negative charge which is neutralized by a single cationic charge; and (iii) the end unit which has one oxygen shared with another  $\text{PO}_4$ , and there are two negative charges. The simplest picture would not take resonance into consideration, so one of the four oxygen atoms in a  $\text{PO}_4$  tetrahedron would be doubly bonded to the phosphorus and would not contribute to the interatomic bonding. The p-d orbital overlap responsible for the  $\pi$ -bond is concentrated primarily between the P atom and its non-bridging oxygen ( $\text{P}-\text{O}^-$ ). If the number of non-bridging oxygen atoms is reduced, then the average degree of  $\pi$ -character of the  $\text{P}-\text{O}$  bonds increases; one effect of such an increase would be to decrease the average  $\text{P}-\text{O}$  bond length [19]. Although the x-ray diffraction results do show that the first peak occurs at about  $1.58 \text{\AA}$ , characteristic of the  $\text{P}-\text{O}$  distance expected for linked  $\text{PO}_4$   $Q^2$  tetrahedra, the determination of the  $\text{P}-\text{O}$  bond length is not of an accuracy sufficient to provide a sensitive measure of the exponent  $n$  in  $Q^n$ . However, metaphosphates of a trivalent-ion modifier  $\text{R}^{3+}$  have the formula  $\text{R}(\text{PO}_3)_3$ . In principle any structure made up of middle groups completely will fit the metaphosphate formula: a metaphosphate structure comprised of chains or rings, with the O/P ratio of 3.0, would be made up of  $Q^2$  tetrahedra. Glasses modified by univalent cations, namely the amorphous alkali metal and silver metaphosphates, are comprised of long chains of interconnected middle  $\text{PO}_4$  tetrahedra [2]. The fractal dimensionality of unity found for amorphous  $\text{AgPO}_3$  [15] is consistent with such a  $\text{PO}_4$  chain structure.

By contrast the fractal bond connectivity of the rare-earth metaphosphate glasses  $\text{R}(\text{PO}_3)_3$  lies between 2.2 and 2.8, indicating that the structure of these glasses is close to having a three-dimensional character [13, 16]. There must be a strong degree of cross linkage, as might be expected for modifier cations whose valence is greater than unity. It seems that there is considerable branching in the  $\text{PO}_4$  skeleton with consequent increase in the number of end and branching units. The coordination numbers (table 4) found

for the rare-earth ions are consistent with this model: rare-earth ions would preferentially occupy interstices formed in the vicinity of branches in the network; this would enable them to bond ionically with this number of surrounding oxygens on PO<sub>4</sub> tetrahedra. These observations concerning the structure add weight to earlier assumptions of a model of a skeleton comprised of PO<sub>4</sub> tetrahedra linked via bridging oxygen atoms to interpret a wide range of vibrational and optical properties of the rare-earth metaphosphate glasses. The chemical durability of these glasses probably results from the enhancement of the extent of chain cross linkage by three-valence rare-earth ions, pinning the network in an almost three-dimensional structure, reducing the susceptibility of the linked PO<sub>4</sub> groups to aqueous attack [16–20]. The x-ray diffraction results support this general model for the rare-earth metaphosphate glasses. In the case of rare-earth oxides of the general type R<sub>2</sub>O<sub>3</sub>, where R is the rare-earth species, the oxygen atoms are situated in an octahedral arrangement about the rare-earth ion. These results suggest that this arrangement may be modified in these glasses to include some higher-coordinated sites.

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