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EXAFS and x-ray structural studies of $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ metaphosphate glass

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Although the metaphosphate glasses $R(PO_3)_3$ containing high concentrations of rare-earth R^{3+} ions have potentially important applications in optical communications and laser technologies, there is little previous information about their structures. To establish the essential features of the structure of such a glass, the complementary techniques of x-ray diffraction and extended x-ray-absorption fine structure (EXAFS) have been used upon the terbium metaphosphate glass, having a composition found by electron probe microanalysis to be $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$. The combination of the two techniques allows for a more comprehensive interpretation of the structural data, since each method suffers from differing analytical problems, notably the composite radial distribution function obtained from diffraction, and the present lack of a good calibrant for the EXAFS experiment. The diffraction results prove to be consistent with a network model dominated by a phosphate glass skeleton constructed from PO_4 tetrahedra bonded to adjacent tetrahedra via bridging oxygen atoms. This previously unestablished structural model has been used formerly to interpret a wide range of thermal, ultrasonic and optical properties. The EXAFS, being an atom-type specific probe, have provided the more direct information on the local structure at the rare-earth ion site in vitreous $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$: notably a strong correlation in 2.25 Å, associated with an average coordination number of 7±1 for oxygen atoms surrounding a Tb^{3+} ion.

I. INTRODUCTION

Glasses doped with small quantities of rare-earth elements have received increasing amounts of attention due to their wide range of novel optoelectronic applications. Silicate systems have attracted most interest due to the great technology advance in fabrication of doped optical fibres of suitable quality for inclusion in industrial systems. Phosphate glass systems have tended to lag behind, partly due to their lower resistance to moisture contamination, which is detrimental to optical performance, and secondly the very success of silicate systems in the field. However it is possible to make phosphate glasses $(R_2O_3)_x(P_2O_5)_{1-x}$, where R represents one of the rare-earth elements La–Lu or Y, where the mole fraction x of rare-earth ions is very large ($x \cong 0.25$).[1–3] These glasses have a range of fundamentally interesting optical, acoustic, nonlinear acoustic, and magnetic properties which show considerable potential for applications in optical data transmission, detection, sensing, and laser technologies.[4,5] During the manufacture of these rare-earth phosphate glasses it has been found that even when the starting charges are varied from 5 to 25 mol % of R_2O_3, the compositions of the end product glasses each turned out to be similar and close to $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$. This corresponds to the stoichiometric metaphosphate composition $R(PO_3)_3$. We have found that these rare-earth metaphosphate glasses $R(PO_3)_3$ are particularly stable to water compared with the corresponding materials made with alkali or transition-metal ions.[1]

The rare-earth dopant incorporated into the glass matrix provides the electronic energy-level structure allowing the manufacture of optical devices such as glass host lasers and optical amplifiers and is the key to some novel magnetic properties. Information about the atomic structure of rare-earth metaphosphate glasses $R(PO_3)_3$ is sparse. The most important feature to establish is the identity of the structural units. To date, most structural studies of binary phosphate glasses have been made on glasses in which the network modifier consist of either monovalent or divalent ions rather than rare-earth ions. The essential structural information which has accrued from these studies has been reviewed by Van Wazer[6] and Martin.[7] For phosphate glasses in general, chains, rings, and branched polymeric units of interconnected PO_4 tetrahedra can be produced by corner sharing oxygen atoms between the tetrahedra. Neglecting resonance, it can be assumed simplistically that one of the four oxygen atoms in a tetrahedron is doubly bonded to the phosphorus and does not take part in the network bonding. There are a number of building units from which phosphates can be constructed. One is the branching PO_4 unit in which three oxygen atoms are shared with neighboring PO_4, units. Another is the middle unit in which two oxygen atoms are shared with neighboring PO_4 and there is one negative charge which is neutralized by a cat-

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ion. Finally in an end unit one oxygen is shared with another PO_4, and there are two negative charges. Pairs of PO_4 tetrahedra can share only one corner via a bridging oxygen atom. If any cation is denoted by M, then all phosphates with a univalent ion modifier can be written as $xM_2O \cdot yP_2O_5$; then a metaphosphate has the composition corresponding to the ratio r, equal to M_2O/P_2O_5, of unity. For a trivalent rare-earth cation M_2O would be replaced by R_2O_3 leading to the metaphosphate $R(PO_3)_3$. In principle, any structure made of middle groups completely will fit the metaphosphate formula; consensus is that the fundamental skeletal structure is probably comprised of long chains of interconnected middle PO_4 tetrahedra, although in fact any closed ring made solely from middle units also satisfies the metaphosphate formula. Furthermore it should be noted that inclusion of an end unit on a chain, can be offset by a corresponding inclusion of a branching unit, still maintaining the metaphosphate stoichiometric balance. To find out how these criteria meet the atomic arrangement in the rare-earth metaphosphate glasses, it is necessary to make detailed structural investigations using probes for different aspects of the structure. To avoid as far as possible complexities involving branching, middle, and end PO_4 units and how their relative numbers might depend upon glass composition, such a study needs to be carried out on a glass with a composition as close as possible to that defined by the metaphosphate formula $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$, which corresponds to $R(PO_3)_3$, Hence, the present study has been concentrated on a glass of formula $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ well-characterized by a wide variety of physical property measurements.

To date, the most instructive information concerning the structure of rare-earth metaphosphate glasses has accrued from use of the high-frequency region of the Raman-scattering spectrum to identify the vibrational modes within the molecular units which comprise the glass network.[1,8-11] Studies of the vibrational modes of phosphate glasses containing Pr^{3+} and Dy^{3+} ions have been carried out using infrared, far infrared,[8] and of binary CeO_2-P_2O_5 and Pr_2O_3-P_2O_5 glasses, using Raman spectroscopy.[9] The Raman spectra of metaphosphate $(Sm_2O_3)_x(P_2O_5)_{1-x}$, glasses are consistent with vibrational motions of structural units comprised of corner linked, PO_4 tetrahedra.[1] Raman spectra obtained for lanthanum,[1] europium,[10,11] and gadolinium[11] metaphosphate glasses closely resemble those of the samarium phosphate glasses,[1] indicating similarity of their basic structure regardless of the rare-earth cation. In general the spectral assignments suggest that PO_4 tetrahedra do comprise the basic skeletal structure of each of these glasses but this conjecture needs to be put on a firmer footing. Greaves *et al.*[12] have applied extended x-ray-absorption fine structure (EXAFS) to construct a modified random network model for mixed lead-iron phosphate glasses in the metaphosphate regime. Their work indicates a structure comprised of metaphosphate chains cross linked by the lead and iron ions. The morphology of the modified regions complement the phosphate chain structure, forming channels that bifurcate through the structure. The iron occupy well-defined octahedral sites, as compared with the lead ions, which have a far more disordered environment. Here we report the use of x-ray diffraction and EXAFS to characterize the local structure of the rare earth in a $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ glass. The experiments were performed at the synchrotron radiation source at the Daresbury Laboratory, UK. The x-ray-diffraction results provide information on the general phosphate glass network, while the EXAFS is a direct probe of the local atomic environment of the terbium atoms.

II. EXPERIMENTAL PROCEDURE

Metaphosphate glasses of general formula $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$ can be made by melting mixtures of the rare-earth oxide with phosphorus pentoxide P_2O_5 in a furnace and then casting into a mold.[1] The major difficulties encountered stem from the elevated temperatures needed, since the melting temperature of these glasses lies in the range 1300–1800 °C. A stoichiometric, well mixed charge comprized of terbium oxide of 99.9% purity and phosphorus pentoxide was first made up and placed in a closed alumina crucible. To react the constituents, the mixture of Tb_2O_3 and P_2O_5 in the crucible was heated in an electrical muffle furnace at a temperature of 500 °C for about 1 h and then the temperature was progressively raised up to 1650 °C. This procedure was adopted so as to ensure melting and mixing the glass thoroughly. Usually the molten glass contained numerous gas bubbles, trapped in the high viscosity mixture. To remove these inclusions, a process of refining was carried out. This consisting of raising the temperature of the molten glass to a higher temperature. (+100 °C) than the melting point, reducing the viscosity and so increasing the rate at which the bubbles rose to the surface. To promote homogeneity, the furnace temperature was decreased and then increased to about 100 °C below and above the melting point several times for periods of about 15 min each, before finally setting it rather above the melting temperature at 1650 °C. After being checked, the melt was cast by pouring as fast as possible into a hot steel split cylindrical mold 10 mm inside diameter and 40 mm long which had been previously heated in an annealing furnace held at the temperature 650 °C at which the glass produced was subsequently to be annealed. After casting, the glass in its mold was immediately transferred to an annealing furnace where it was kept for 48 h to relieve any residual stresses, which could cause embrittlement. In particular, the glass must not contain any appreciable residual stress which is likely to result in breakage during cutting and polishing. At the end of this annealing process, the furnace was switched off and the glass left to cool down to room temperature gradually by controlled thermal treatment at a cooling rate of 0.5 °C/min.

Glass compositions were determined using an electron probe microanalyzer fitted with wavelength dispersive spectrometers. A pure single crystal of $Tb_3Fe_5O_{12}$ was used as a standard. Regardless of the starting constituent ratios, glass formation occurs when as a consequence of volatilization of P_2O_5 the metaphosphate glass composition range has been reached, nominally 25 mol % rare-earth oxide.[10] This was true for the terbium phosphate glasses. To characterize the glasses further, their elastic properties have been measured by the ultrasonic pulse-echo overlap technique and optical absorption, Raman spectra, and magnetic susceptibility have been determined. The elastic constant results are compared with those of samarium and europium metaphosphate glasses in Table I. The glasses modified by terbium are rather denser than their samarium or europium analogs, in accord with the lanthanide contraction. They are also rather stiffer, having a somewhat larger bulk modulus. Laser fluorescence studies have established that the terbium ion is trivalent in this glass; further details of this and of other optical and acoustic properties of these terbium phosphate glasses will be published elsewhere.

The glass used for the diffraction and EXAFS experiments was powdered, by crushing between two steel plates and subsequently using an agate mortar and pestle, this glass powder then being dusted onto tape for easy mounting in an x-ray beam. Care was taken to avoid water contamination, although experiments were not performed under dry air or vacuum conditions. Analysis using the fast Fourier infrared absorption technique has shown that the water content of these rare-earth metaphosphate glasses is less than 0.1 mol %.[11]

The x-ray-diffraction and EXAFS experiments, were performed at the SRS, Daresbury Laboratory, UK, in the former case using a high intensity line with the synchrotron radiation being produced through a 5-T superconducting wiggler. The diffraction experiment was performed in a $\theta/2\theta$ transmission geometry, and at an x-ray wavelength of 0.5 Å. This geometry was chosen as it simplifies many of the necessary corrections. The 2θ angular range measured was chosen to be 2° to 130° in 0.2° steps giving a nominal k range $[k=(4\pi\sin\theta)/\lambda]$ of 0.4 to 23 Å^{-1}, although the data was of limited statistical quality beyond $k\approx 21$ Å^{-1}. The EXAFS spectrum was taken in standard transmission mode at the Tb L_{III} edge, giving an approximate analyzable EXAFS k range of 2–11 Å^{-1}. This corresponds to a diffraction k range of 4–22 Å^{-1}, due to the $2k$ dependence of the EXAFS theory. The same sample was used for both the diffraction and the EXAFS experiments.

III. DATA TREATMENT AND ANALYSIS

The diffraction data were corrected for beam polarization, variations in incident flux, background scattering effects and sample illuminated volume variation on rotation. The correction and normalization procedures adopted were those described by Huxley,[13] based upon an iterative method of constrained fitting of the absorption, incoherent or Compton scattering, and the self-scattering parameters. General data analysis is based upon the text by Warren.[14] The structure function $i(k)$ is obtained by the relationship:

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

where I_{eu} is the corrected intensity function (scaled to electron units), N is the number of scattering units (uc) in the sample [in this work the base unit was chosen to be of metaphosphate stoichiometry, $R(\mathrm{PO_3})_3$] scaled to 1, 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:

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

where ρ_e is the average electron density of the sample, $\sum_{\mathrm{uc}} Z_j$ is the total number of electrons in the scattering unit, and $w(k)$ an applied window function to suppress transform ripple caused by the finite range of the data.[15] For this particular analysis, the function applied is

$$w(k)=\begin{cases} 1-3(k/k_{\max})^2\ , & |k|<k_{\max}/3 \\ 3/2[1-2|k/k_{\max}|+(k/k_{\max})^2]\ , & k_{\max}/3<|k|<k_{\max}\ . \\ 0 & |k|>k_{\max}. \end{cases} \tag{3}$$

TABLE I. Properties of terbium phosphate $(\mathrm{Tb_2O_3})_x\ (\mathrm{P_2O_5})_{1-x}$ glasses in comparison with those of the samarium and europium analog.

Property	Terbium phosphate $(\mathrm{Tb_2O_3})_x\ (\mathrm{P_2O_5})_{1-x}$ glasses				$(\mathrm{Sm_2O_3})_x(\mathrm{P_2O_5})_{1-x}$	$(\mathrm{Eu_2O_3})_x\ (\mathrm{P_2O_5})_{1-x}$
Composition x	0.226	0.247	0.263	0.271	0.224	0.252
Density (kg/m^3)	3435	3501	3578	3666	3280	3438
Elastic stiffness (N/m^2) C_{11}^S	73.9	74.8	76.2	78.3	66.4	70.4
C_{44}^S	24.2	25.4	25.7	25.3	23.6	23.2
Bulk modulus (N/m^2) B_0^S	41.6	40.9	42.0	44.5	34.9	39.5
Fractal dimension $(4C_{44}^S/B_0^S)$	2.33	2.48	2.45	2.27	2.71	2.35
Debye temperature θ_D	363 K	366 K	364 K	359 K	363 K	353 K

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

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

where

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

Data analysis proceeds by calculation of the P_{ij} for various r_{ij} with known atom-type pairings, such as P-O and Tb-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 distances r_{ij} in the scattering unit of comparison. Due to the complex nature of the composite distribution function $t(r)$ obtained from a single diffraction experiment, independent information is necessary if physically meaningful information is to be extracted from the data. Here this is supplied by the EXAFS data taken on the same system. Since $t(r)$ is a function representing the electron density variations within the system, it is often difficult to interpret meaningfully. However if the first few peaks in the function at low r are independent, a reasonable estimate of coordination numbers can be made. If these low r peaks are not isolated features, this becomes a very difficult procedure. The criteria 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.

Absolute determination of a suitable, accurate scattering unit from which to scale the diffraction data is extremely difficult, on account of P_2O_5 volatilization losses during manufacture of the glass. Constituent ratios have been chosen to be those determined by the electron microprobe $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ which were close to the metaphosphate stoichiometry $Tb(PO_3)_3$. Uncertainties in estimating component ratios can have serious effects on the determination of the atomic self-scattering function $\sum_{\mathrm{uc}}f_j^2$. However, in this case the microprobe data give credence to the adoption in our analysis of the metaphosphate composition $Tb(PO_3)_3$, and we are confident that the associated base unit of composition is a good approximation.

The EXAFS data analysis was performed using the standard Daresbury Laboratory EXAFS analysis suite of programs, notably EXCALIB, EXBACK, and EXCURV90,[16] which, respectively, perform the tasks of

(i) Summation of multiple data sets and calibration of their edges and absorptions.

(ii) Background subtraction and normalization of the EXAFS signal.

(iii) Fitting of the EXAFS spectrum by means of the fast curved wave theory.[17,18]

Since no suitable standard samples were available at the time of the EXAFS experiment, calibration of the sample dependent parameters in the EXAFS model, notably the amplitude reduction factor $A(k)$ accounting for inelastic-scattering effects damping the EXAFS signal, was not possible.[19] To allow for this, larger errors are quoted for the evaluated coordination numbers N_i. In spite of this, valuable information is still accessible. Examination of the phenomenological plane wave equation, which can be used to describe the EXAFS spectra, establishes the relationships between parameters

$$\chi(k)=A(k)\sum_i\frac{N_i}{kR_i^2}|f(k,\pi)_i|\sin(2kR_i+2\delta+\varphi_i)$$
$$\times\exp\left[\frac{-2Ri}{\lambda}\right]\exp[-2\sigma_i^2k^2] \ . \qquad (6)$$

In EXAFS, $\mathbf{k}$ is the wave vector of the freed photoelectron. Note the direct correlation in the two variables $A(k)$ and N_i. $A(k)$ typically varies between 0.7 and 0.9, depending upon the atomic number of the excited atom type, but is also somewhat dependent upon the data normalization procedures. If no calibrant system is available, this range of values can give a crude estimate of the possible variation in N_i. The other parameters in this expression are R_i, the distance between the excited atom and the neighboring electron backscattering atom i, $f(k,\pi)_i$ is a measure of the strength of backscattering of the atom type i, δ is the phaseshift induced in the electron wave as it propagates through the excited atom potential, whilst φ_i is the phaseshift induced by the backscattering atom potential, λ is a mean free path term to account for the finite lifetime of the propagating electron wave, and σ is the exponent in the Debye-Waller term to account for static and vibrational disorder in the structural system under examination.

The plane-wave equation is a very crude model for EXAFS and is not used in the EXCURV90 code,[16] which uses the far more reliable fast curved wave theory[17,18] or the small atom approximation.[20]

IV. RESULTS AND DISCUSSION

Figure 1 shows the fit of the diffraction intensity profile corrected for experimental effects (solid line), to the atomic self-scattering (broken line) determined for the metaphosphate unit of composition $Tb(PO_3)_3$. The quality of this fit corroborates the chemical composition of the glass determined by the electron probe microanalysis as metaphosphate.

The $i(k)$ and $t(r)$ derived from the diffraction data are shown in Figs. 2 and 3. Our attribution of the first and second features in $t(r)$ is summarized in Table II. The peak positions and areas were determined by fitting a series of Gaussians to the data, Fig. 3. The first peak at 1.58 Å is characteristic of the P-O distance expected for phosphate glass systems thought to consist of linked PO_4 tetrahedra. For example, in the studies of other phosphate glasses the P-O distance was determined as 1.55 Å (Ref. 21) and 1.6 Å.[22] The area of the first peak, when fitted with the appropriate pair function P_{ij} (Fig. 4), is found to be consistent with a value of approximately 24 for N_{ij}, the total number of P-O and O-P correlations;

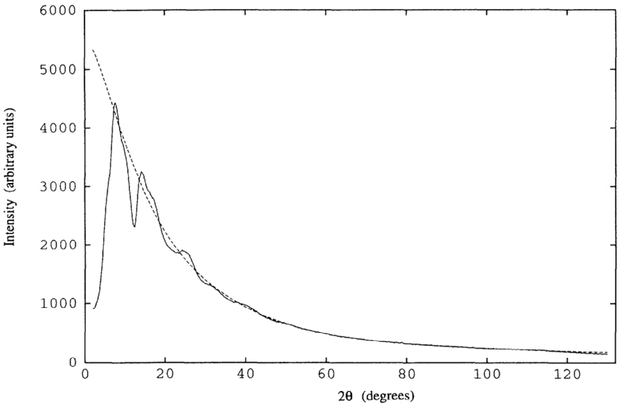

FIG. 1. Terbium metaphosphate glass, diffraction (solid line), and self-scattering (broken line).

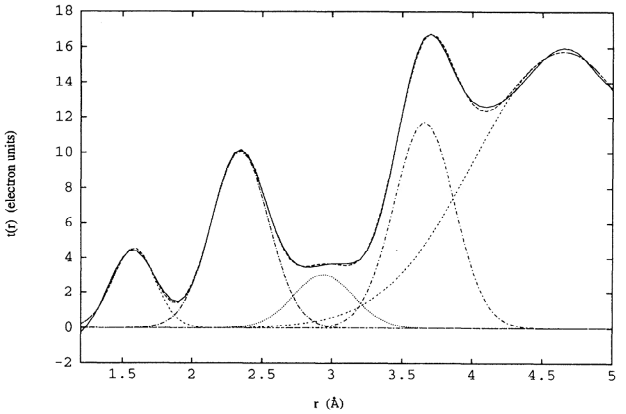

FIG. 3. $t(r)$ (solid line) and fit (broken lines) obtained from $i(k)$.

this is consistent with the $R(PO_3)_3$ unit of a metaphosphate glass and a fourfold coordination of oxygens about each of three phosphorus atoms.

The second distance at 2.34 Å is slightly more difficult to assign being a combination of both Tb-O and O-O correlations. The O-O distance has been shown to be 2.50 Å in previous studies[21] of transition-metal-doped phosphate glasses, but in the present case, due to the dominant contribution of the terbium-oxygen correlation and the lack of peak resolution, individual assignments cannot be made. If the second peak in the diffraction $t(r)$ where only due to O-O correlations, it would be much smaller than that observed as can be seen from the diffraction pair functions, Fig. 4. The area of the second peak was evaluated, again by the fitting of calculated pair correlation functions P_{ij}, Fig. 4, for Tb-O and O-O combinations, resulting in a value, $N_{ij} \approx 18$, i.e., a total of 18 Tb-O and O-Tb correlations which is consistent with a coordination arrangement of about nine oxygen atoms about each terbium atoms. This approximate calculation was made ignoring the O-O contribution to the second peak and it therefore represents an upper bound to the coordination number. Coordination numbers of this magnitude are reasonably common amongst rare-earth compounds due to the ionic nature of the bonding that these ions experience.

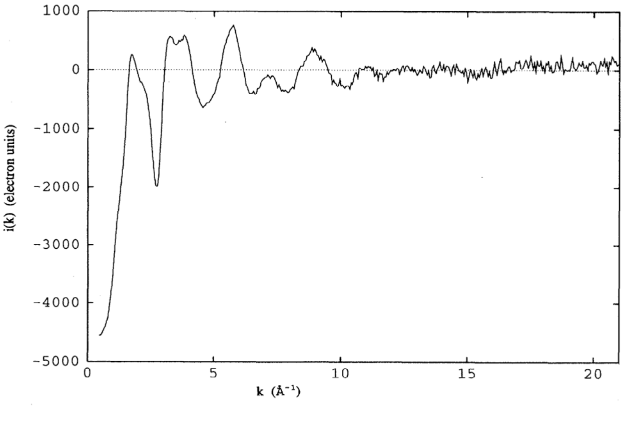

FIG. 2. $i(k)$ obtained for terbium metaphosphate glass.

The resolution of features in the distribution function suffers somewhat from the need for a window function $w(\mathbf{k})$ in the Fourier transform. However, the actual positions, i.e., interatomic distances, of the observed peaks were stable regardless of window function applied and are reliable to ±0.05 Å.

The EXAFS data (Figs. 5 and 6) are dominated by the Tb-O first shell correlations; the results obtained from a two shell fit are given in Table III. The first Tb-O distance of 2.25 Å is consistent with the assignment of the combination of the correlations in the diffraction data, and the coordination of 7.0±1 supports the calculation of the strength of the correlation observed for the second peak in the diffraction data. A second Tb-O correlation at 3.92 Å is visible with a coordination of 4.1±1, this feature being far weaker than the first shell, although found to be statistically significant by the criteria of Joyner, Martin, and Meehan.[23]

A consideration of the coordination number ≈7, for the first shell of oxygen atoms about the terbium atom suggests that the rare-earth ions occupy a mixture of sites varying between pseudooctahedral and body-centered-cubic nature corresponding to coordination numbers of 6 and 8, respectively, since EXAFS only probes mean values within the system. A coordination of six oxygen atoms arranged octahedrally about the rare earth is consistent with the atomic arrangement found in a rare-earth oxide of the form R_2O_3, and given the uncertainty associated with our determination of the coordination number

TABLE II. X-ray-diffraction results obtained on the $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ glass.

Sample	Peak position (Å)	Atomic correlation(s) assigned
$(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$	1.58±0.05	P-O
	2.34±0.05	Tb-O and O-O

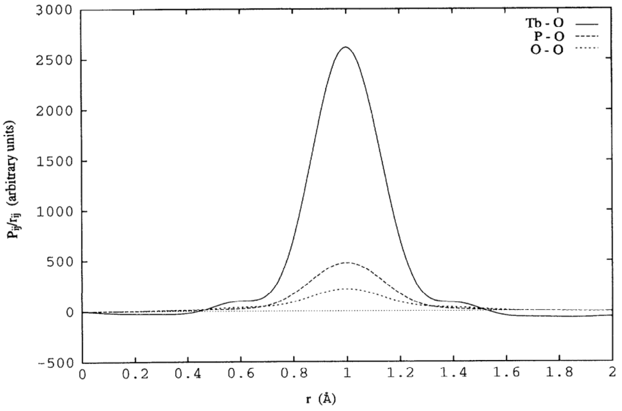

FIG. 4. Pair functions (P_{ij}/r_{ij}) calculated for various atomic correlations.

$N(\pm 1$ atom) we have no reason to suspect another arrangement in these samples.

The variance of the bond distribution σ^2 is relatively large, suggesting a distribution in the Tb-O first shell distance, a situation not unexpected in glasses. The EXAFS spectrum shows no evidence for any Tb-Tb correlations within the short-range order, an important result when considering both the possible optical and magnetic properties of the glass. This suggests that the terbium ions are relatively well spaced throughout the bulk phosphate network.

These EXAFS results were obtained using only a single scattering theory, since for first shell correlations, multiple scattering can be ignored. The errors quoted in Table III are purely statistical in nature, evaluated from correlation parameters between the variables used in the data fitting process. In particular the coordination numbers and Debye-Waller factors, are difficult to determine accurately in the absence of any calibration system, to determine the value of $A(k)$. A more realistic estimate of the errors in the coordination number being ±1 atom. The values for interatomic distance are in general much more reliable, although the actual error in evaluated distance is more likely to be of the order of ±0.05 Å due to "second order" errors introduced by the lack of calibrant.

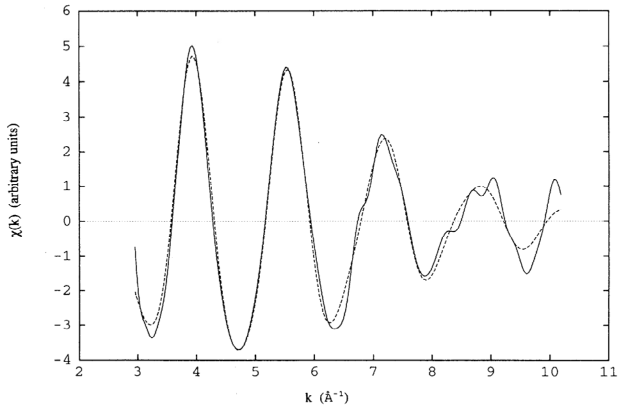

FIG. 5. EXAFS spectra (solid line) and theoretical fit (broken line).

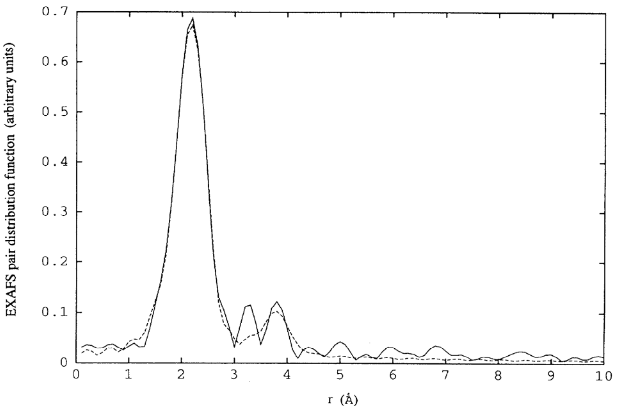

FIG. 6. Fourier transform of EXAFS spectra (solid line) and theoretical fit (broken line).

The fundamental unit of the terbium metaphosphate glass has been shown to be the PO_4 tetrahedron. In the case of metaphosphates made from univalent ions such as alkali ions or silver ions it appears that the fundamental skeletal structure is comprised of long chains of interconnected middle PO_4 tetrahedra. The atomic environments determined here are consistent with such a structural model for the terbium metaphosphate glass. Some light on the connectivity of the network can be shed by reference to the fractal dimension determined from the elastic property measurements (Table I). By considering a two-dimensional (2D) Sierpinski gasket as the fractal object in a study of the critical behavior of a random, d-dimensional, isotropic, elastic medium, Bergman and Kantor[24] have shown that the effective fractal dimensionality d of an inhomogeneous random mixture of fluid and a solid backbone at threshold is given by $4C_{11}/B$. The fractal dimension d should vary from $d=3$ for 3D networks of tetrahedral coordination polyhedra to $d=2$ for 2D structures and to $d=1$ for 1D chains, enabling Bogue and Sladek[25] to associate it with the connectivity of glass networks. The fractal dimensionality d of close to unity obtained for a pure $AgPO_3$ metaphosphate glass[25] is consistent with a structure comprised of weakly linked chains of PO_4 tetrahedra. In contrast the fractal dimensionality of the rare-earth metaphosphate glasses $R(PO_3)_3$ is closer to 2.5 (Table I), which implies more crosslinkage as anticipated for modifier cations whose valence is greater than unity, or increased branching of the network of PO_4 chains possibly facilitated by an in-

TABLE III. Structural parameters determined from the EXAFS results obtained on the $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ glass.

Atom type	Coordination No. atoms	Distance (Å)	σ^2 (Å^2)
Oxygen	7.0±0.2	2.25±0.002	0.014±0.0004
Oxygen	4.1±0.8	3.92±0.009	0.015±0.003

crease in the number of end and branching units incorporated into the base phosphate network. This agrees with the coordination numbers found from the structural studies. The model of a network of polymeric chains of PO_4 tetrahedra linked via bridging oxygen atoms has been used previously to interpret a wide range of thermal, ultrasonic, and optical properties of the rare-earth metaphosphate glasses with reasonable success.[1–3,8–10] The strong cross linking may also account for the stability of and nonhygroscopic nature of the rare-earth phosphate glasses.

The diffraction and EXAFS results also provide information about the kind of site occupied by the terbium atoms. In rare-earth oxides generally, i.e., R_2O_3, where R is the rare-earth species, the oxygen atoms are situated in an octahedral arrangement about the rare-earth ion. The EXAFS results obtained would suggest that this arrangement be modified to include some higher coordinated sites, such as a body-centered-cubic arrangement centered upon the terbium ion. Computer modeling of the metaphosphate glass structure including incorporation of these rare-earth sites into the phosphate glass matrix is now needed.

V. CONCLUSIONS

(1) A combined study using the complementary of x-ray-diffraction and EXAFS techniques of the terbium metaphosphate glass of composition $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$ has established that the network is constructed from PO_4 tetrahedra.

(2) The atom-type specific EXAFS probe has provided direct information on the local structure at the rare-earth ion site in vitreous $(Tb_2O_3)_{0.26}(P_2O_5)_{0.74}$: notably a strong correlation at 2.25 Å, associated with an average coordination number of 7±1.

(3) There is no evidence for clustering of the terbium ions within the glass, at least on the length scales probed by EXAFS.

(4) The fractal dimensionality of the metaphosphate glasses $M(PO_3)_3$ is about 2.5, indicating that an increased degree of branching of the metaphosphate chains is present, this glass having a more three-dimensional nature to its structure than vitreous silver metaphosphate.

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