Coordination of Eu^{3+} Ions in a Phosphate Glass by X-ray Diffraction

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Two vitreous samples, 0.9 $Zn(PO_3)_2 \cdot 0.1\ Eu(PO_3)_3$ and pure zinc metaphosphate, were examined by X-ray diffraction to determine the local environment of the Eu^{3+} ion. Using a difference procedure involving the radial functions of the two glasses, the results indicate that the rare-earth ion is surrounded on average by a polyhedron of about 7.4 oxygens at 2.36 Å and about 1.6 oxygens at 2.68 Å. A possible different coordination of the zinc ion in the two samples, suggested by the experimental findings, is discussed.

Key words: X-ray diffraction, Structure of glasses, Rare-earth ions phosphates.

Introduction

Knowledge of ionic coordination in oxide glasses is important for understanding their atomic structure and various related physical properties [1, 2]. In the case of rare-earth ions having luminescent properties, this information is strongly sought, because the electronic spectra are sensitive to changes in the local environment of the dopant [3, 4]. Ionic coordination of rare-earth ions in melts and glasses is also important in models describing crystal-melt partition coefficients, which are valuable indicators of geochemical processes [5, 6].

Optical spectroscopy and crystal field analysis have been often used to probe the local structure of luminescent ions in glass, mainly after the advent of the fluorescence line narrowing technique (FLN) [3, 7]. The inhomogeneously broadened profile of the absorption band is probed with a narrow linewidth tunable laser. The Eu^{3+} ion has been extensively investigated by this technique because of the relative simplicity of its energy level structure, which reduces the ambiguity in the interpretation. The FLN spectrum of Eu^{3+} in a complex silicate glass has been interpreted by Brecher and Riseberg [8] in terms of a structural model in which the rare-earth ion is surrounded by eight equidistant coordinating oxygens arranged in a distorted antiprism with C_{2v} symmetry, with a ninth oxygen approaching the central ion along the C_2 axis. This model agrees with the spectral properties of Eu^{3+} ions in $Ba(PO_3)_2$, $Zn(PO_3)_2$ and $Pb(PO_3)_2$ glasses [9]. Some difference in the Eu^{3+} spectral parameters was observed in the three glasses and was ascribed to differences in the local fields of the Eu^{3+} sites induced by the three network modifiers (Ba, Zn, Pb) [9, 10].

Unfortunately, in the case of other ions and other energy level structures, the FLN technique is far more ambiguous, and different coordination schemes can lead to reasonable agreement with derived experimental spectral parameters. For the same Eu^{3+} ion a different coordination picture (sixfold) and a different symmetry (C_1 point group) were shown to be consistent with the spectral features of Eu^{3+} doped lead metaphosphate glass by a computational method that couples molecular dynamics simulation and parameterized point-charge crystal-field calculations [11]. Furthermore, the model by Brecher and Riseberg was

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shown to fail with respect to the analysis of FNL data of an alkali-modified silicate glass, that is, Eu^{3+} doped $Na_2Si_2O_5$ [12]. Investigations by other experimental probes are therefore needed to obtain a clearer description of rare-earth ions coordination.

Local order phenomena in glasses have been extensively investigated by X-ray and neutron diffraction and, more recently, by EXAFS spectroscopy [1, 2]. In many cases these methods have been able to describe the average local environment of both network former and modifier cations. However, investigations on rare-earth ions are very scarce. Two groups of studies can be mentioned. In the first one the short range order of various rare-earth ions (Ho, Er, Eu, Gd, Tb) in the form of amorphous hydrous oxides has been investigated by X-ray diffraction [13–15]. In the second one, the determination of the environments of La^{3+}, Tb^{3+}, Gd^{3+}, Er^{3+} in silicate glasses has been attempted by EXAFS [16–18]. Both types of studies meet with some difficulties. With X-ray diffraction, the main problem consists in the evaluation of pair contributions from total radial functions; with EXAFS, coordination numbers come out rather uncertain, especially in samples with only traces of rare-earth ions. In any case, the results of these investigations cannot be used to generalize the ionic environments found in oxide glasses, since the coordination of rare-earth ions in glasses is likely to change within wide limits when the chemical surrounding is changed, similarly to what is observed in crystalline structures [16].

Recently we have determined the coordination of various transition metal ions in several glassy matrices using a difference X-ray diffraction method, in which diffraction data from a metal free reference glass are subtracted from those of the sample of interest [19–21]. We now wish to extend the same procedure to the study of rare-earth ions in phosphate glasses. As a first approach to this extensive study we choose to investigate the coordination of Eu^{3+} in a zinc metaphosphate glass.

Experimental

Two metaphosphate glasses were prepared by a melt quenching procedure described in detail in a previous paper [9]. In the first sample, Zn is the only metal present, in the second 10 percent of Zn^{2+} ions were substituted by Eu^{3+}. The densities of the two samples, measured by the immersion method, are 2.80 and 2.87 g/ml, respectively.

The absorption and luminescence spectra of cut and polished samples of Eu-doped zinc phosphate glass were measured at room temperature using a Perkin Elmer Lambda 15 spectrophotometer and a Perkin Elmer LS 50 corrected fluorimeter, respectively.

XRD data were obtained by placing the glasses in the form of thin slabs in a Seifert $\theta - 2\theta$ X-ray diffractometer [19–21]. The radiation from a Mo tube was monochromatised by reflection on a LiF crystal. The angular region $4° < 2\theta < 116°$ was divided into about 260 intervals; using a step scan preset time method, at least 40,000 counts were collected at each point. The measurements were performed at room temperature. The observed intensities were corrected for background, absorption and polarization and were normalized by the semiempirical method proposed by Habenschuss and Spedding [22].

From the normalized intensities I_{eu}, structure functions $i(s)$ were obtaining according to

$$i(s) = I_{eu} - \sum n_i f_i^2(s), \tag{1}$$

and radial distribution functions $D(r)$ were then evaluated by Fourier transformation:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_{s_{min}}^{s_{max}} s \cdot i(s) \cdot M(s) \cdot \sin(sr)\, ds, \tag{2}$$

where r is the interatomic distance, n_i are the stoichiometric coefficients of the assumed unit containing m atom types, f_i are the scattering factors of the species i. ϱ_0 is the average electronic bulk density, and $M(s)$ is a modification function of the form

$$M(s) = \left\{ \frac{[\sum n_i f_i(0)]^2}{[\sum n_i f_i(s)]^2} \right\} \exp(-ks^2), \tag{3}$$

where $k = 0.005$ [19–21, 23–25]. No correction for spurious peaks was applied. In the assumed units the coefficient 1 was assigned to the P atom. Since the precision of the difference method is strongly dependent on the accuracy of the experimental work, alignment of the X-ray apparatus, counting statistics and experimental data treatment were kept rigorously constant for the sample pair.

Results

The low-resolution electronic absorption and luminescence spectra of the Eu^{3+}-doped glass are found to be identical to the corresponding spectra of the $Zn(PO_3)_2$ glass doped with 2.5 mol% of $Eu(PO_3)_3$

described in [9]. The decay curves of the emission from the $^5D_0$ state are exponential with a lifetime of 2.3 ms, identical to the one obtained for the more dilute glass [9]. These observations seem to indicate that no strong clustering of the Eu^{3+} ions occurs in the glass under investigation. This assures that structural information obtained for Eu^{3+} in the more concentrated glass can be transferred to the glass doped with 2.5 mol% of $Eu(PO_3)_3$.

Experimental structure functions and corresponding radial distribution functions are plotted in Figs. 1 and 2, respectively. Both function pairs appear very similar. In the radial curves spurious ripples at low r are small and very similar; this is a proof that systematic errors have been minimized and are the same in both cases. Three peaks are evident, though not completely resolved, centered at 1.55 Å, 2.00 Å and 2.55 Å. They can be easily ascribed to P–O, Zn–O and O–O pairs on the basis of known phosphate crystal structures and ionic radii of the species involved. In particular, the value of 1.55 Å is very close to the average P–O separation within the PO_4 groups, which are the basic building blocks of the phosphate glasses, and the average O–O distance in PO_4 tetrahedra comes out equal to about 2.50 Å [23–24].

At longer r values, a strong peak is observed at about 3.3 Å. Indeed, different contributions could fall in this region, originating from the atoms of the vitreous network interacting with themselves or with the metal ions. However, the peak prominence suggests that it should be mainly caused by interactions involving the heavy metal atoms.

The interactions between Eu^{3+} ions and their surrounding atoms do not give rise to new resolved peaks. However, the third peak at about 2.50 Å in $D(r)$ of the Eu^{3+} doped glass is higher than it is in $D(r)$ of Zn metaphosphate. This is the distance range where Eu^{3+}–O bond lengths fall in crystalline structures [13–16]. The contributions from the interactions of Eu^{3+}-ions can be evidenced by subtracting the radial curve of Zn metaphosphate from that of the Eu-containing glass. In fact, the contributions from the phosphate network should cancel out by this operation, as both glasses have the metaphosphate composition. The result of this procedure is reported in Figure 3. The first peak shows a maximum at about 2.5 Å, close to the expected Eu^{3+}–O distance; it has a broad and asymmetrical shape, indicating that the distribution of local environments of the Eu^{3+} ions does not stem from a regular polyhedron. A second peak is present

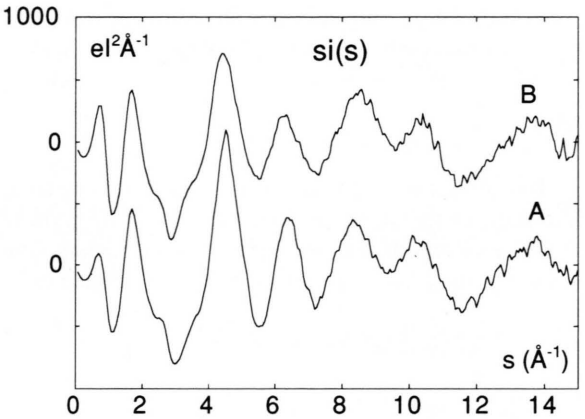

Fig. 1. Structure functions of the vitreous samples: $Zn(PO_3)_2$ (A) and 0.9 $Zn(PO_3)_2$ · 0.1 $Eu(PO_3)_3$ (B).

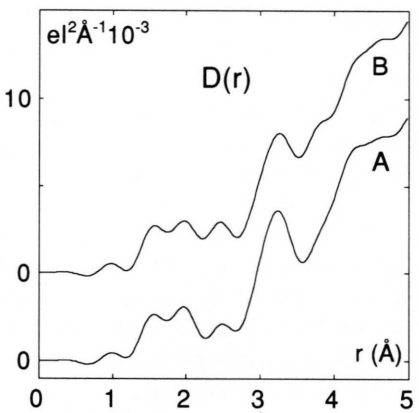

Fig. 2. Radial distribution functions of the vitreous samples: $Zn(PO_3)_2$ (A) and 0.9 $Zn(PO_3)_2$ · 0.1 $Eu(PO_3)_3$ (B).

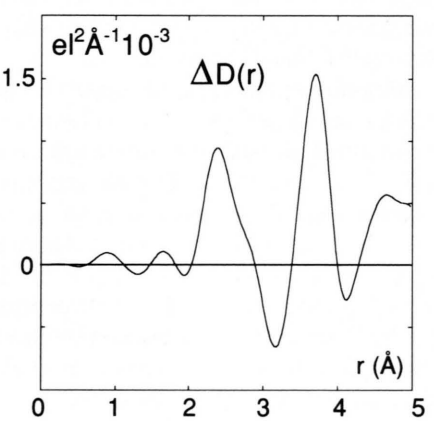

Fig. 3. Differential radial functions $\Delta D(r)$ obtained subtracting the radial function of the matrix $ZN(PO_3)_2$ from the same function of the Eu-containing glass.

at about 3.70 Å and indicates that the order around Eu^{3+} extends beyond the first coordination shell.

Discussion

To obtain quantitative information about the coordination of the europium ions, the Eu^{3+}–O peak at 2.5 Å was simulated by Fourier transforming pair contributions to the structure function, defined as

$$2n_{Eu} \cdot f_{Eu} \cdot f_O \cdot N_{Eu\text{-}O} \cdot \left[\frac{\sin(s r_{Eu\text{-}O})}{s r_{Eu\text{-}O}}\right] \cdot \exp\left[-\left(\tfrac{1}{2}\right) \cdot \sigma^2_{Eu\text{-}O} \cdot s^2\right]; \quad (4)$$

here, $r_{Eu\text{-}O}$ is the average distance between atoms Eu and O, $\sigma_{Eu\text{-}O}$ is the associated root mean squares deviation, and $N_{Eu\text{-}O}$ is the average number of oxygen atoms surrounding an europium atom [19–21, 23–25]. To account for the asymmetrical shape of the Eu^{3+}–O peak, two contributions were introduced in the simulations, with different distances, frequency factors and root mean squares deviations. Varying the six independent parameters, the theoretical peak was matched in a satisfactory fashion to the experimental one, as shown in Figure 4. The final parameters are reported in Table 1. The figures in parentheses represent limit errors, estimated by taking into account possible errors in stoichiometric coefficients, uncertainties in the peak fitting criteria and correlation between σ and N parameters [19–21].

The results in Table 1 are in very good agreement with literature data. In fact, although Eu^{3+} is in the middle of the rare-earth ions series, it belongs to the group of large rare-earth ions, for which a coordination number greater than 6 is expected [26]. This expectation is largely fulfilled in crystalline structures; in fact, Eu coordination numbers in the range 7–9 have been found in a great variety of geometrical situations, because the intermediate and large rare-earth cations have multiple site types and also low site regularities [16]. Coordination numbers in the same range have been found for the larger rare-earth ions in glasses and amorphous oxides by XRD and EXAFS [13–17]. It is worth mentioning that the present result compares well with the Eu^{3+} environment proposed by Brecher and Riseberg [8] and adopted by Capobianco et al. [9] for the same kind of glass investigated here.

Although the result seems to be quite reasonable, some questions still arise because of unexpected features appearing in two different regions of the difference curve $\Delta D(r)$. Firstly, in the distance interval between the first and second peak of $\Delta D(r)$ a negative peak is evident, which suggests an imperfect balance of the two starting radial functions in this region. Secondly, the negative feature expected around 2 Å in the $\Delta D(r)$ is missing; this negative contribution should have appeared since both glasses have metaphosphate stoichiometry but the zinc content in the mixed sample is lower than that present in the other glass. A possible explanation of these facts consists in an other mean coordination of Zn^{2+} ions in the Zn–Eu mixed metaphosphate than in pure Zn metaphosphate. To verify this hypothesis, the coordination of Zn^{2+} ions was also determined by simulating in the s-space the contribution to the structure function of the Zn–O interactions, together with those coming from the $P–O_4$ tetrahedra. For this, a procedure described in [21, 23, 25] was followed. The radial functions where the three main peaks fall (from 1.20 to 2.70 Å) were backtransformed to s-space, and the "partial" structure functions obtained were then used as references. The theoretical contributions described in terms of physical parameters, r, N, and σ were then fitted to the reference curves by a least squares algorithm; in the

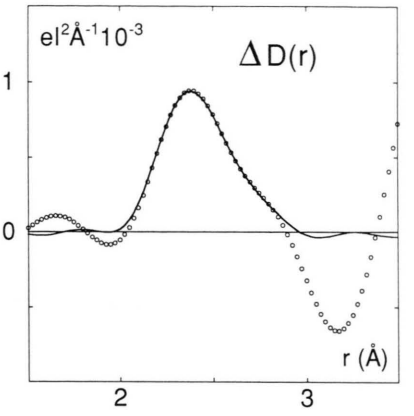

Fig. 4. Experimental (circles) and simulated (line) peak of Eu-O interactions in the differential radial function.

Table 1. Coordination parameters for europium-oxygen interactions obtained by simulation of the difference curve. Estimated errors are given in the parentheses.

r_1	σ_1	N_1	r_2	σ_2	N_2
2.365(5)	0.12(1)	7.4(2)	2.680(5)	0.08(1)	1.6(2)

case of the Eu^{3+}-doped glass, the contribution of $Eu^{3+}-O$ interactions was also introduced, transferring the structural parameters reported in Table 1 and refining them only in the final stages of the fitting procedure. From the very good best-fit curves obtained, the coordination number of Zn^{2+} turned out greater in the Eu-doped glass (about 4.6 against 4.2), explaining why in the difference radial function no negative Zn–O peak was observed. Meanwhile, P–O distances and coordination numbers came out very close (1.53 Å and 4.0 neighbours) to the values expected for the PO_4 group [23–24], thus verifying the correctness of the experimental data and of the analysis. The number of O–O contacts, $N_{O\text{-}O}$, came out greater than that expected on the basis of the infinite chain model usually adopted for metaphosphate glasses [27–29]; the term at issue must account for tails from longer distance contributions which were not explicitely introduced in the simulation. Finally, the parameters describing $Eu^{3+}-O$ pairs were very similar to those obtained in the simulation of the difference curve. The variation of zinc coordination can also partially explain the negative region around 3.2 Å in the difference curve, as a different number of $O_{Zn}-O_{Zn}$ and Zn-second neighbours are present in the two glasses; moreover, part of the Zn–Zn interactions falling in the same range should disappear in the doped sample, to be replaced by Eu–Zn at a longer distance.

It is worth noting that the variation of $N_{Zn\text{-}O}$ with the composition is not surprising, as many properties of Zn phosphate glasses show discontinuities at the metaphosphate composition [30–31]. A discontinuity in the Zn–O coordination number was also observed by EXAFS spectroscopy [32]. The behaviour is probably the reason of apparent discrepancies in assessing the Zn coordination in different glasses of the same nominal composition $Zn(PO_3)_2$. In fact, on the basis of diffractometric experiments, some authors proposed coordination numbers equal to 4 [33–35], as in the present study. But other determinations, based on XRD and anomalous X-ray scattering measurements led to $N_{Zn\text{-}O}$ around 5 [24, 36]. Small deviations from the metaphosphate composition, often coupled with some differences in the preparation procedure, are the probable cause of important differences in density and in the short range order. It is not surprising then that the substitution of an appreciable amount of Zn^{2+} by Eu^{3+} ions at this composition may give rise to variations of Zn coordination. In any case, the values found for $N_{Zn\text{-}O}$ are in the range defined for this quantity by the previous determinations, and there is no reason not to accept them.

In conclusion, we have obtained a picture which appears absolutely reasonable; on the other hand, the differences in zinc coordination (including $O_{Zn}-O_{Zn}$ distances) do not seem to affect the peak due to Eu–O interactions, as they appear in a region of the radial curve rather distant (about 0.4 Å) from the abscissa of the maximum of the peak of interest.

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