

A Neutron and X-ray Diffraction Study of the Structure of Nd Phosphate Glasses

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Diffraction experiments were performed on two $(\text{Nd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses for studying the environmental order of the Nd^{3+} cations. In case of the metaphosphate glass ($x = 0.25$) a combination of X-ray and neutron diffraction data was used to separate the Nd-O and O-O first neighbor peaks. An Nd-O coordination number of 6.6 ± 0.3 and a mean Nd-O distance of (0.239 ± 0.001) nm were determined. In the ultraphosphate glass studied ($x = 0.20$) these values increase to 6.9 ± 0.3 and (0.240 ± 0.001) nm where the Nd-O coordination number is equal to the number of terminal oxygen atoms (O_T) which are available for coordination of each Nd^{3+} cation. This indicates the formation of NdO_n polyhedra not sharing any O atom where also all O_T 's are in Nd- O_T -P positions. In the metaphosphate glass the NdO_n polyhedra have to share some O_T sites.

Key words: Neutron Scattering; X-ray Scattering; Short-range Order; Phosphate Glasses.

1. Introduction

Various properties of the phosphate glasses make them advantageous for being host materials of lanthanide oxides Ln_2O_3 in applications for lasers or magneto-optical devices [1]. One of the network-modifying cations for laser applications is the Nd^{3+} cation [2, 3] where, typically, Nd_2O_3 is a minor fraction among other modifier oxides. The environmental order and the distances between the Nd sites are an essential factor for the optical properties [2]. Small widths of a fluorescence line of Eu^{3+} sites in sodium phosphate glasses as host materials, if compared with those of other glass-forming systems, indicate a small variety of the environments of the Eu^{3+} sites [4]. This behavior may be due to the large flexibility of the surrounding oxygen sites. Also binary Ln phosphate glasses can be prepared which have large Ln_2O_3 fractions of up to 25 mole%. Some unusual magnetic properties were detected for several of these phosphate materials [5].

The diffraction study here presented is focussed on binary Nd phosphate glasses where two samples of different Nd_2O_3 fractions were used. The most stable glasses are obtained in a range close to the metaphosphate composition where long chains and ring structures of corner-linked PO_4 units exist. The structural units and their connectivities are well investigated by vibrational spectroscopy or by ^{31}P nuclear magnetic resonance (NMR) spectroscopy (cf. [6]). For studying the oxygen coordination of the Ln^{3+} cations, neutron and X-ray diffraction (ND and XRD) experiments or extended X-ray absorption fine structure (EXAFS) spectroscopy are applied [7–15]. A decrease of the Ln-O first-neighbor distances along with the increase of the electron number of the Ln species was shown by EXAFS for the glasses $(\text{Ln}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ with x varying in a range from 0.19 to 0.26 [8, 12, 15]. Though some of the Ln-O coordination numbers, N_{LnO} , obtained vary from 5 to 8, a decrease from 6.5 for N_{LaO} to 6.0 for N_{ErO} is suggested [12], which is also concluded from the behavior of the Ln-O

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distances. A number N_{LaO} of seven was found in a combination of XRD and ND data of a LaP_3O_9 glass [10].

A further question concerns the effects of N_{LnO} when the composition x is varied. For two different Ce phosphate glasses an N_{CeO} of six and no essential change were detected, as reported in [15]. These findings differ from the behavior of the N_{LnO} 's which is known for the related crystal structures. The number N_{NdO} is eight in $\text{NdP}_5\text{O}_{14}$, and it changes to six in NdP_3O_9 crystals [16]. But two additional O sites exist in NdP_3O_9 at Nd-O distances larger by 0.03 nm, which are not found in LnP_3O_9 crystals of the smaller Ln^{3+} cations such as in ErP_3O_9 [17]. The N_{LnO} 's of eight and six in $\text{LnP}_5\text{O}_{14}$ and LnP_3O_9 crystals are equal to the numbers M_{TO} of terminal oxygen atoms (O_T) which are available to coordinate each of the Ln^{3+} cations. Consequently, the O_T 's occupy positions in P-O_T-Ln bridges and the LnO_n polyhedra do not share any of their O_T atoms. Thus, the Ln sites are separated by PO_4 units. First, such specifics were detected for phosphate glasses of the bivalent metal oxides MeO. Most of the anomalies of their glass properties could be attributed to these effects [18]. The changes of the N_{ZnO} and N_{MgO} numbers which were detected in the ultraphosphate range [19 - 21] are due to a stabilization of those MeO_n polyhedra which do not share in the use of the O_T 's. In this process, the doubly-bonded O_T 's of the threefold-linked PO_4 units tend to coordinate an Me site too [18].

A first case of a change of the Me-O coordination number of a trivalent Me site was found by ^{27}Al NMR in the $(\text{Al}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses with x of about 0.33 [22]. The decrease of N_{AlO} from 5.3 to 4.8 when Al_2O_3 is added behaves as M_{TO} . Similar changes for the Ln-O coordination numbers in $(\text{Ln}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses are expected in a compositional range between $x = 0.16$ and 0.25 according to N_{LnO} numbers between eight and six. The number M_{TO} is calculated with $M_{\text{TO}} = (1 + 2x)/x$ [22]. The Nd-O coordination numbers of Nd phosphate glasses of two different compositions will be determined by the diffraction studies presented here. Since the Nd-O first-neighbor distance superposes with the lengths of the O-O edges of the PO_4 tetrahedra, a combination of ND and XRD data is advantageous to separate the two contributions. The XRD experiment is more important for a determination of N_{NdO} due to the large X-ray scattering power of Nd atoms if compared with those of the other constituents.

2. Experimental

2.1. Sample Preparation

The raw materials in the preparation of the Nd phosphate glasses were Nd_2O_3 and H_3PO_4 , where ratios of 1:10 and 1:6 were used in the 'as batch' compositions. The mixtures were melted in silica crucibles at temperatures of 1400 to 1450 °C. According to the analysis of the P fraction and to a comparison of the IR spectra, the compositions of the final $(\text{Nd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses were estimated to $x \cong 0.20$ and 0.25. The samples which are slightly different in their red color are labelled NdP4 and NdP3 according to the ratios $n(\text{Nd})/n(\text{P})$. Since the melting temperatures are high, a significant amount of SiO_2 or Al_2O_3 of crucible material can have entered the glass sample such as considered in [13, 14]. Good information about the real glass compositions is needed for the analysis of the diffraction data. The use of vibrational spectroscopy for our samples gives a sufficient measure to obtain the degree of network depolymerization. Part of the P_2O_5 content of the NdP4 sample was lost due to evaporation. Also some effort was made to minimize the water contamination [23]. The use of sealed ampoules is recommended to avoid moisture attack and the loss of P_2O_5 for melting ultraphosphate samples of even smaller Nd_2O_3 fractions [24]. The mass densities were measured by the Archimedes principle using CCl_4 . Values of 3.14 and 3.31 g/cm³ were obtained for the NdP4 and NdP3 samples, which correspond to number densities of atoms of 69.0 and 68.0 nm⁻³. Since only a very small amount of the sample NdP4 was available, an ND experiment of NdP4 was not possible.

2.2. Diffraction Experiments

The XRD experiments were performed on the BW5 wiggler beamline at the DORIS III synchrotron (Hamburg/Germany), where an energy of 130 keV ($\lambda = 0.00954$ nm) of the incident photons was used. Powdered sample material was loaded into silica capillaries of 2.0 mm diameter with a wall thickness of 0.01 mm. During the measurements the specimens were positioned in a vacuum vessel to suppress air scattering. Since the scattering angles are small, the transmission factors are assumed to be independent of the angle. The angular increment in the step-scan mode was 0.05°. In the 2θ -range from 0.35° to 9°

an absorber was set in the diffracted beam to avoid counting rates higher than 10^5 s^{-1} . The other scans range from 8° to 25° . Details of such experiments and the corrections are described in [25]. The electronic energy window of the solid-state Ge-detector was chosen to pass the elastic line and the full Compton profile but no fluorescence scattering. The dead-time corrections were made with $\tau = 2.4 \mu\text{s}$. A fraction of 0.91 of the incident photons is polarized horizontally. Both numbers allow to merge the data of the scans obtained for both angular ranges and with different synchrotron currents. Corrections are made for background, container scattering, and absorption. The scattering intensities are normalized to the structure-independent scattering functions which have been calculated by polynomial fits of the tabulated atomic parameters of the elastic and the Compton scattering data [26]. Finally, the Compton fractions are subtracted and Faber-Ziman structure factors, $S_X(Q)$, are calculated [27].

The ND experiments of the NdP3 glass were performed on the time-of-flight instrument SANDALS of the pulsed neutron source ISIS at the Rutherford Appleton Laboratory. The powdered sample was loaded into a thin-walled vanadium cylinder of 5 mm diameter with a wall thickness of 0.025 mm. The absorption and multiple scattering corrections are made by the ATLAS program suite [28]. The self scattering contributions are calculated according to the compositions of the samples where inelasticity effects are small due to the small scattering angles of SANDALS. The scattered intensities recorded in the various detector groups and normalized to separate self terms are merged to the differential scattering cross-section. Large resonance terms of the epithermal neutrons with the Nd nucleus limit the momentum transfer, Q_{max} , to about 250 nm^{-1} with $Q = 4\pi/\lambda \sin \theta$. The incoherent scattering is subtracted and the total neutron structure factor, $S_N(Q)$, is calculated [27].

3. Results

The structure factors of the two samples measured are shown in Figure 1. Due to the use of high-energy photons (130 keV) the $S_X(Q)$ functions are available up to 290 nm^{-1} . The data of both samples are similar to each other except of the shoulder at 20 nm^{-1} . The low- Q feature, another shoulder at 11 nm^{-1} , is already known for the $S_X(Q)$ data of a LaP_3O_9 glass [10]. The neutron $S_N(Q)$ function of the NdP_3O_9

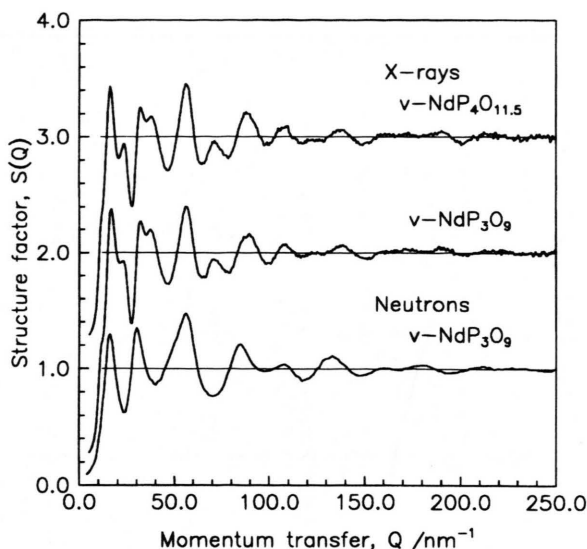


Fig. 1. Structure factors, $S(Q)$, of the two glasses studied obtained by XRD and for the NdP_3O_9 glass additionally obtained by ND experiments. The upper functions are shifted for clarity.

glass is very similar to that of the Nd phosphate glass of $x = 0.187$ measured by Cole *et al.* [13], and also to that of the LaP_3O_9 glass [10]. The ND data [10, 13] obtained on the LAD instrument* reach a Q_{max} of 500 nm^{-1} . The smaller range of scattering angles available on the SANDALS instrument requires the use of neutrons of higher energies. Thus, the effects of the Nd resonances are obtained at smaller Q which limits the Q -range of our data. Note that XRD experiments possess much weight in the determination of the N_{NdO} 's. The weighting factors of the partial $S_{\text{NdO}}(Q)$ and $S_{\text{OO}}(Q)$ functions in the $S_X(Q)$ data of the NdP3 sample are 0.276 and 0.165 while in the $S_N(Q)$ data the weighting factors are 0.142 and 0.481, respectively.

The correlation functions, $T(r)$, are obtained by Fourier transformation (FT) with

$$T_k(r) = 4\pi r \rho_0 + \frac{2}{\pi} \int_0^{Q_{\text{max}}} Q [S_k(Q) - 1] \cdot M(Q) \sin(Qr) dQ, \quad (1)$$

where ρ_0 is the number density of atoms. $M(Q)$ is a damping function, that according to Lorch [29] with $M(Q) = \sin(\pi Q/Q_{\text{max}})/(\pi Q/Q_{\text{max}})$ being applied.

*The LAD instrument at ISIS is dismantled and replaced by the more powerful instrument GEM.

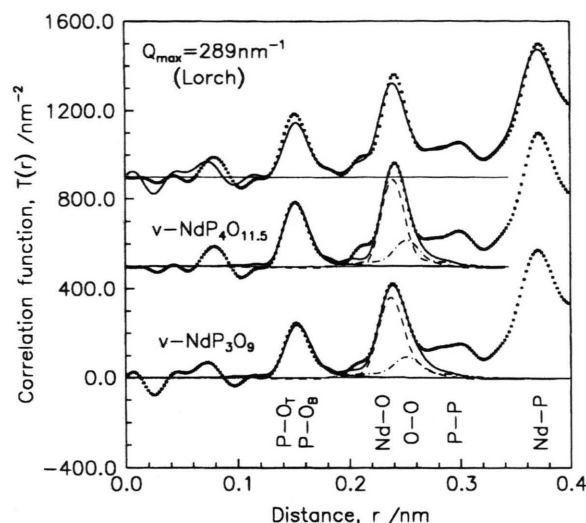


Fig. 2. On top, the correlation functions, $T_X(r)$, of the glasses NdP3 (solid line) and NdP4 (dotted line) are compared in the range of the first three distance peaks. Below, the experimental $T_X(r)$ data of the glasses NdP4 and NdP3 (dotted lines) are compared with the fitted model functions (solid lines). Additionally, the partial model functions are shown as peaks already weighted according to concentration and scattering power and broadened due to the effects of damping and Q_{\max} with the contributions P-O (solid lines), Nd-O (dashed lines), and O-O (dash-dotted lines). The P-O model peak is almost identical with the first P-O peak (cf. Fig. 3). The upper functions are shifted for clarity.

The parameter k is either X or N for the XRD and ND data. The $T(r)$ functions are shown in Figs. 2, 3, where the Q_{\max} 's used are indicated in the plots. The $T_X(r)$ functions are compared in Figure 2. All three peaks visible in the NdP4 data (dots) are higher than those in the NdP3 data (line). Since $N_{\text{PO}} = 4$ is not changed and the P fraction in NdP4 is larger than in NdP3, the P-O peak must be higher for the NdP4 sample. On the other hand, since the Nd fraction is smaller in NdP4, the Nd-O and Nd-P peaks are expected to be smaller due to weighting factors of 0.246 and 0.160 smaller than 0.276 and 0.172 for NdP3. But the decrease is overcompensated by an increase of N_{NdO} and N_{NdP} , which explains the increase of the Nd-O and Nd-P peaks.

The N_{NdO} 's are determined by Gaussian fitting. The effects of the damping function and the truncation at Q_{\max} in the FT procedures are taken into account by a method described in [30]. Thus, also Q -dependent weighting factors are applied in case of the X-ray data [30]. For fitting the $T(r)$ data the Marquardt algorithm [31] is used, where coordination numbers, mean

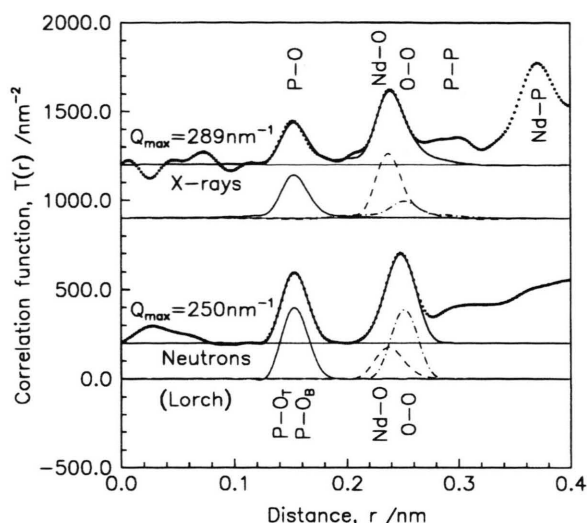


Fig. 3. Comparison of the experimental $T_X(r)$ and $T_N(r)$ data (dotted lines) of the NdP3 glass with the model functions (solid lines). Separately, the partial model functions are shown as peaks already weighted according to concentration and scattering power and broadened due to the effects of damping and Q_{\max} with the contributions P-O (solid lines), Nd-O (dashed lines), and O-O (dash-dotted lines). The upper functions are shifted for clarity.

distances and full widths at half maximum (fwhm) are the parameters of the model Gaussian functions. Two Gaussian functions are used for fitting the P-O peak with the P-O_T and P-O_B contributions (O_B-bridging oxygen atom). A split P-O peak was found for other phosphate glasses by ND experiments of high resolving power ($Q_{\max} \approx 500 \text{ nm}^{-1}$) [32]. The ratios of the fractions of the P-O bonds are fixed in the fits according to the degree of network depolymerization, which is determined by the compositions. The difference of the mean P-O_T and P-O_B bond lengths is fixed to 0.011 nm. A possible asymmetry of the Nd-O peak is approximated using two Gaussian functions, which does not imply the existence of two Nd-O distances. Some of the six parameters have to be fixed (Table 1). No information of a second Nd-O peak at 0.27 nm, such as it exists in the NdP₃O₉ crystal [16], can be given. Due to peak overlapping in the concerning distance range such Nd-O distances cannot be extracted from total $T(r)$ data. The fifth Gaussian function approximates the O-O peak. All resulting peak parameters are given in Table 1. Only the combined fit of ND and XRD data of the NdP3 glass allows to extract the O-O contributions (Fig. 3). The O-O coordination number depends on the degree of network depoly-

Table 1. Parameters of the Gaussian functions which result from the fit of the first-neighbor peaks. The distances and full widths at half maximum (fwhm) are given in nm. The parameters marked by asterisks were fixed during the fit. Their choice is explained in the text. The errors given in parentheses are estimated according to the reproducibility of the parameters after the data corrections and the Gaussian fitting.

| Sam- ple | Atom pair | Coordi- nation number | Distance | fwhm | Total coordin. number | Mean distance |
|-------------|------------------|-----------------------------|------------|----------|-----------------------------|------------------|
| NdP3 | P-O _T | 2.10(10) | 0.1490(5) | 0.009(3) | 4.2(2) | 0.1545(10) |
| | P-O _B | 2.10(10) | 0.1600(5) | 0.016(4) | | |
| | Nd-O | 4.7(4) | 0.2360(15) | 0.019(3) | 6.6(3) | 0.2395(15) |
| | | 1.9(3) | 0.2480* | 0.030* | | |
| | O-O | 4.07(20) | 0.2515(15) | 0.020(3) | | |
| NdP4 | P-O _T | 1.73(10) | 0.1470(5) | 0.004(3) | 3.95(20) | 0.1532(10) |
| | P-O _B | 2.22(10) | 0.1580(5) | 0.015(4) | | |
| | Nd-O | 5.5(4) | 0.2385(15) | 0.017(3) | 6.9(3) | 0.2405(15) |
| | | 1.4(3) | 0.2480* | 0.030* | | |
| | O-O | 4.17* | 0.2515* | 0.019(3) | | |

merization with $N_{\text{OO}} = 24/(5 + y)$ [19] where, y is the ratio $n(\text{Ln}_{2/3}\text{O})/n(\text{P}_2\text{O}_5)$ with $y = 3x/(1 - x)$. N_{OO} is expected to be four for the NdP3 glass with $y = 1$ or $x = 0.25$. Actually, $N_{\text{OO}} = 4.07$ is obtained from the fit, which is a good agreement. For the NdP4 glass an N_{OO} of 4.17 is calculated. Together with the O-O distance ($r_{\text{OO}} = 0.2515$ nm) this value is fixed in the fit of the $T_{\text{X}}(r)$ data of the NdP4 glass. The model functions which correspond to the P-O, Nd-O, and O-O distances are shown in Figs. 2 and 3, as well. Figure 2 illustrates that Nd-O coordination numbers cannot be obtained from the $T_{\text{X}}(r)$ data without assumptions about the O-O peak. Figure 3 shows the combination of the $T_{\text{X}}(r)$ and $T_{\text{N}}(r)$ data. The $T_{\text{N}}(r)$ data are excellently fitted while the $T_{\text{X}}(r)$ data show unreasonable features at 0.21 nm and below 0.1 nm. The increase of N_{NdO} from 6.6 (NdP3) to 6.9 (NdP4) is accompanied by an increase of the mean r_{NdO} by only 0.001 nm, whereby the asymmetry of the peak is reduced. The changes lie in the uncertainty limit of XRD experiments. However, due to the use of the same experimental conditions for both samples we would interpret the increase of N_{NdO} in the NdP4 glass as a real change. Since every O atom in an NdO_n polyhedron is also a corner of a PO_4 tetrahedron, the increase of N_{NdO} is accompanied by an increase of N_{NdP} . The linkage of an Nd site with a PO_4 tetrahedron by edges is an unfavourable situation [18]. The increase of the Nd-P peak for the NdP4 sample, which is visible in Fig. 2, is explained by this increase

of N_{NdP} because the weighting factor even decreases from 0.172 to 0.160. An exact determination of the Nd-P coordination number from the total $T(r)$ data is not possible.

4. Discussion

Commonly, the oxygen coordination numbers of the network-modifying cations in oxide glasses are not expected to vary much. Changes in the number of oxygen atoms supplied for their coordination may cause such effects. The number of O_T atoms per modifier cation, M_{TO} , is large in phosphate glasses. In a first line, the O_B's do not participate in this process. The number M_{TO} may even equal the oxygen coordination number of a modifier cation [18]. This situation suggests that all O_T's could have exactly one modifier neighbor, and no modifier cation, here the Nd³⁺ cations, would have to share an oxygen neighbor with a further Nd³⁺ site. For threefold-charged cations M_{TO} equals $(1 + 2x)/x$ [22]. Thus, the NdP4 and NdP3 glasses studied with $x = 0.20$ and 0.25 can form the described glass structures with Nd-O coordination numbers of seven and six. The number N_{NdO} of 6.9 ± 0.3 of the NdP4 glass (Table 1) is equal to $M_{\text{TO}} = 7$ which allows the formation of NdO_n polyhedra not sharing any O_T sites. All O_T's can have one Nd neighbor. The individual numbers n are presumably not only seven, but a distribution with numbers six, seven and eight is formed. Diffraction experiments yield mean coordination numbers. For the sample NdP3 the N_{NdO} observed, 6.6 ± 0.3 , is larger than six. The building principle of separate NdO_n polyhedra is not realised, though the decrease of M_{TO} induces a small decrease of N_{NdO} . The situation for the NdP_3O_9 crystal [16] is similar, where the two O sites at 0.270 nm in addition to the six at 0.236 nm indicate that a structure with only NdO_6 octahedra is not stable and the NdO_n polyhedra share in some O_T neighbors. Consequently, some smaller Nd-Nd distances should occur which do not exist in the NdP4 glass and which may have effects on the optical properties. Reverse Monte Carlo simulations of the structure of a LaP_3O_9 glass [10] revealed a few short La-La distances of 0.45 nm which belong to LaO_n polyhedra sharing in an O_T while a larger number of La-La distances of about 0.65 nm is due to a separation by a common PO_4 neighbor. The smaller of the lanthanide cations can form structures with coordination numbers of six also in their metaphosphate

glasses [12, 17], thus with separate LnO_6 octahedra. In the ultraphosphate range the formation of separate LnO_n octahedra is possible for all Ln^{3+} cations such as found for Nd^{3+} in the NdP4 sample with an N_{NdO} of about seven.

When the change of N_{NdO} in accordance with M_{TO} is discussed, the question about the reasons for this process arises. In a first line, the phenomenon should be attributable to principles of charge compensation. Two tendencies may be important [18]: all O_T sites, also those of the threefold-connected PO_4 branching units, aspire to coordinate a modifier cation. Such neighbors would weaken the π -character of the P-O_T bond, this effect being known from Raman spectra [6]. Secondly, LnO_n polyhedra whose vertices are all connected with corners of PO_4 tetrahedra and not with vertices of other LnO_n polyhedra can form more spherical clouds of countercharge which is favoured against any sharing of O_T sites with other Ln's. Therefore, the Ln-O coordination number is changed to equal M_{TO} , the number of which depends on the modifier content (see above). This phenomenon appears in a definite compositional range according to the possible coordination states of the modifier cation. The two samples studied show the transition from a glass with separate NdO_n polyhedra (NdP4) to a glass with some sharing of O_T sites between the NdO_n polyhedra (NdP3). The formation of more symmetric NdO_n polyhedra in phosphate glasses is also made easy by the high flexibility of the O_T sites. The PO_4 tetrahedra in the glasses studied are connected by only two or

three corners, in NdP3 only by two corners. The PO_4 tetrahedra can be orientated as needed.

5. Conclusions

Diffraction experiments were performed on two $(\text{Nd}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses with $x = 0.20$ and 0.25 . In case of the metaphosphate glass (0.25) the combination of X-ray and neutron diffraction data allowed to separate the Nd-O and O-O first neighbor peaks and to determine an Nd-O coordination number of 6.6 ± 0.3 and a mean Nd-O distance of 0.239 ± 0.001 nm. Similar numbers, somewhat larger than six, were also published for the metaphosphate glasses of other lanthanide cations of similar dimension. In the ultraphosphate glass studied ($x = 0.2$) somewhat larger Nd-O coordination number of 6.9 ± 0.3 is detected, which is equal to the number M_{TO} of terminal oxygen atoms (O_T) available for coordination of each modifier cation. This situation allows the formation of NdO_n polyhedra not sharing any O atoms where also all O_T 's are in Nd- O_T -P positions. The study of compositional changes of N_{NdO} requires samples whose compositions are well known. Their preparation is difficult especially in the ultraphosphate range where moisture, crucible material and phosphate evaporation can affect the melt compositions.

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