

Short-Range Order Details of Metaphosphate Glasses Studied by Pulsed Neutron Scattering

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Details of the short-range order of the binary metaphosphate glasses AlP_3O_9 and PbP_2O_6 and the ternary glass system $\text{ZnO-MgO-2P}_2\text{O}_5$ have been studied by pulsed neutron scattering which provides a measuring range up to about $Q_{\text{max}} = 500 \text{ nm}^{-1}$. The splitting of the P–O peak in the distance correlation functions attributable to the different bond lengths for the non-bridging and bridging oxygens was found to decrease with increasing field strength of the network-modifier cations. For the ternary system $\text{ZnO-MgO-2P}_2\text{O}_5$ the peak in the distance correlation function, $T(r)$, produced by the first oxygen neighbours around Zn^{2+} and Mg^{2+} was separated by the additional use of the X-ray structure factor. The distances r_{ZnO} and r_{MgO} extracted from the separated peaks are slightly different from those obtained from the binary glasses ZnP_2O_6 and MgP_2O_6 . The metal-oxygen coordination numbers were found to be $N_{\text{ZnO}} = 4.5$ and $N_{\text{MgO}} = 5.5$. For the two binary systems the coordination numbers Al–O and Pb–O were obtained to be 7 and 5, respectively.

Key words: Pulsed neutron scattering, phosphate glasses, short-range order.

1. Introduction

In diffraction experiments, the measuring range required for the discrimination of two bond lengths different in distances by a value d , is determined by the amount of the peak broadening in the $T(r)$ function caused by the upper termination limit, Q_{max} , of the Fourier transformation. The width of the corresponding peak broadening is $\sim 3.79/Q_{\text{max}}$ [1]. In order to reduce this effect, a shorter wavelength, λ , of radiation can in fact enlarge the magnitude of the scattering vector, $Q (= 4\pi/\lambda \sin \theta)$, whereas the maximum scattering angle 2θ is limited in its range. The diffraction experiment with pulsed sources using neutrons of thermal and epithermal energies provides the scattering of a sample up to about $Q_{\text{max}} = 500 \text{ nm}^{-1}$. If the structural data of Al, Zn, Pb, and Na polyphosphate crystals [2–5] are considered, it becomes obvious that the difference between the P–O bond length for the bridging and non-bridging oxygen atoms is about 0.01 nm. Hence, in order to resolve this small distance difference in the real space, the measuring range must be extended up to Q -values of about 380 nm^{-1} .

The PO_4 tetrahedron is the basic building block constituting the phosphate glass networks. This is linked with its neighbours by at most three P–O–P bridges. The incorporation of network-modifier oxide leads to a change in the ratio of bridging oxygens (BO) to non-bridging oxygens (NBO) due to the decreasing number of links. At metaphosphate composition two links per tetrahedron are formed, which is confirmed by the ^{31}P magic angle spinning (MAS) NMR [6]. By using neutron diffraction experiments, Suzuki and Ueno [8] succeeded in discriminating the two different types of P–O bond existing in a sodium metaphosphate glass, i.e. the larger bond length between the phosphorus and the BO's and the distance between the phosphorus and the NBO's. The difference between the values of the two bond lengths was found to be about 0.014 nm.

Raman scattering measurements on Al, Mg, Zn, Ca, and Na metaphosphate glasses [7] have shown that the P–O as well as the P–O–P vibration frequencies are affected by the kind of network-modifier cations located in the vicinity of the NBO. Shifts and a broadening of the lines were observed with increasing field strength of the cations. The observations were explained by changes of the ionicity of the P–O bond

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caused by a shift of the electron density in direction of the network-modifier cations.

The results just mentioned stimulate to employ pulsed neutron scattering experiments for studying phosphate glasses containing network-modifier cations of higher field strength. The aim of this paper is to determine exact coordination numbers and distances of atom pairs of the glasses AlP_3O_9 , PbP_2O_6 , and $\text{ZnO-MgO-2P}_2\text{O}_5$, which in consequence will allow to discuss changes of the P–O bond character and details of the Me–O coordination spheres.

For the aluminum metaphosphate glass, sixfold Al–O coordination was found by using X-ray and neutron diffraction of moderate resolution ($Q_{\text{max}} = 200 \text{ nm}^{-1}$) [10] but ^{27}Al MAS NMR measurements [11] have given evidence for the occurrence of small amounts of four- and fivefold coordinated Al positions in addition to the AlO_6 units. Diffraction experiments with high resolution provide the possibility to separate the Al–O peak from the neighbouring P–O peak. From the results, an answer can be given whether or not the same coordination number in the Al–O environment is extracted from diffraction methods and ^{27}Al MAS NMR experiments.

The Pb–O coordination in the lead metaphosphate glass was examined by using X-ray diffraction [12] and EXAFS at the Pb L_{III}-edge [13]. From the first experiment $N_{\text{PbO}} = 5$ was obtained, and from the second $N_{\text{PbO}} \approx 8$. An asymmetric bonding in the Pb–O spheres with values N_{PbO} of about 8 (4 atoms in contact and 4 more distant positions) was found in lead silicates with large PbO content [14], whereas in the PbP_2O_6 crystal [4] the Pb^{2+} ion is surrounded by 7.5 oxygen atoms forming a broad Pb–O peak.

The application of different kinds of radiation, e.g. the use of neutrons and X-rays [10], may help to discriminate the peaks produced by the Mg–O and Zn–O distances in the $T(r)$ function obtained from the glass $\text{MgO-ZnO-2P}_2\text{O}_5$. It is of much interest whether the oxygen environment of the Mg^{2+} and Zn^{2+} ions, being equal in dimension but different in electronegativity, is different from that found for the binary glassy systems MgP_2O_6 and ZnP_2O_6 [9, 10].

2. Experimental

2.1. Preparation of glass samples

The raw materials used were sintered metaphosphates prepared from analytical grade carbonates and

phosphoric acid (85%). The glasses were melted in silica crucibles for 30 minutes in air at 1920 K for the AlP_3O_9 glass, 1175 K for the PbP_2O_6 glass, and 1475 K for the $\text{ZnO-MgO-2P}_2\text{O}_5$ glass. The compositions determined by analysis are

$$1.035 \text{ Al}_2\text{O}_3 - 3 \text{ P}_2\text{O}_5 \text{ (2.612 g/cm}^3\text{)} \\ \text{and } 0.94 \text{ ZnO} - 0.83 \text{ MgO} - 2 \text{ P}_2\text{O}_5 \text{ (2.651 g/cm}^3\text{)}.$$

In case of the lead phosphate glass the nominal composition $\text{PbO-P}_2\text{O}_5$ (4.88 g/cm^3) was used. The mass densities are given in parentheses. The melts were cast into moulds of dense graphite and subsequently annealed to room temperature (rate: 10 K/min).

2.2. Diffraction experiments

The neutron diffraction of the glasses was measured with the liquids and amorphous diffractometer (LAD) using the neutron spallation source ISIS of the Rutherford Appleton Laboratory, Chilton, England. 14 detectors were positioned in the interval of the scattering angle 2θ between 5° and 150° . The grain shaped glass samples were filled into thin walled vanadium containers of 11 mm diameter and about 70 mm height and measured in a vacuum chamber. A vanadium rod of 10 mm diameter was used to obtain the primary energy spectra of the neutron source. The data were corrected by standard procedures [15] for attenuation, multiple scattering, inelasticity effects, and for container and background scattering separately for each of the scattering angles. The normalization turned out to be a difficult procedure with the consequence that the data of some of the detectors were omitted. But all parts of the final differential scattering cross sections represent a result averaged from at least two conformable curves of different detector positions.

The X-ray diffraction experiments on the ternary zinc magnesium metaphosphate glass were performed between $Q_{\text{min}} = 4 \text{ nm}^{-1}$ and $Q_{\text{max}} = 200 \text{ nm}^{-1}$ for AgK_α radiation by using a horizontal goniometer as described in [9]. The grain shaped sample was measured in a sealed capillary made from silica with about 1 mm diameter.

3. Results

The neutron structure factors $S(Q)$ shown in Fig. 1 were calculated from the differential scattering cross

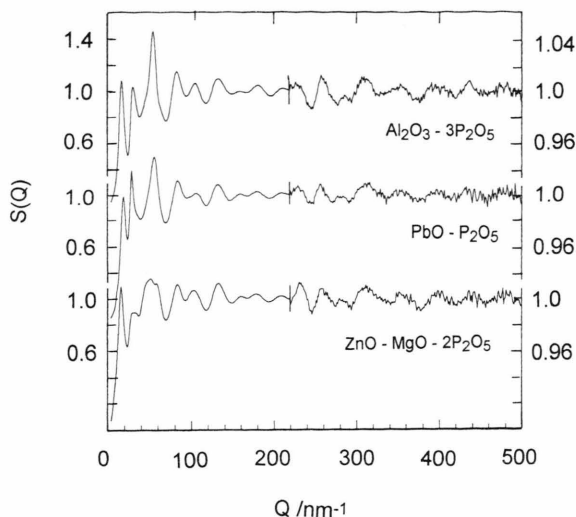


Fig. 1. Experimental neutron structure factors, $S(Q)$, of the metaphosphate glasses studied. The oscillations are enlarged by a factor of 10 beyond $Q = 220 \text{ nm}^{-1}$.

sections $d\sigma/d\Omega$ using the formula

$$S(Q) = \frac{d\sigma/d\Omega - \langle b^2 \rangle}{\langle b \rangle^2}, \quad (1)$$

where b is the neutron scattering length, and $\langle \dots \rangle$ denotes the mean value taking into account the sample composition and the isotopic mixture. For better visibility, the $S(Q)$ curves in Fig. 1 have been multiplied by a factor of 10 for $Q \geq 220 \text{ nm}^{-1}$.

Figure 2 shows the $\text{Diff}(r)$ curves for the glasses studied. These functions, which represent the difference between the radial distribution $\text{RDF}(r)$ and the factor determined by the mean density of atoms ρ_0 , are given by

$$\begin{aligned} \text{Diff}(r) &= \text{RDF}(r) - 4\pi r^2 \rho_0 \\ &= \frac{2r}{\pi} \int_0^{Q_{\max}} [S(Q) - 1] \sin(Qr) Q dQ. \end{aligned} \quad (2)$$

For extracting the short-range order parameters, the distance correlation function $T(r) = \text{RDF}(r)/r$ has proved to be more useful.

Procedures for analysing the $T(r)$ function were described by Wright [16]. This technique is based on the approximation of the peaks in $T(r)$ by a sum of Gaussian curves, which are multiplied with the weighting factors of the appropriate atom pairs and folded with so-called peak shape functions [16] in order to take into account the termination effect. In this

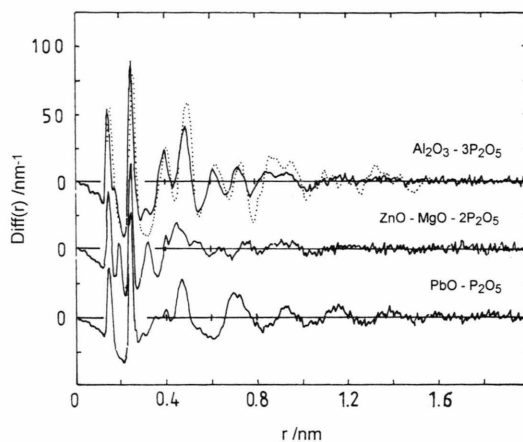


Fig. 2. Difference functions of radial distributions for the phosphate glasses studied. The curve of AlP_3O_9 glass is compared with that (dotted line) of vitreous SiO_2 [24].

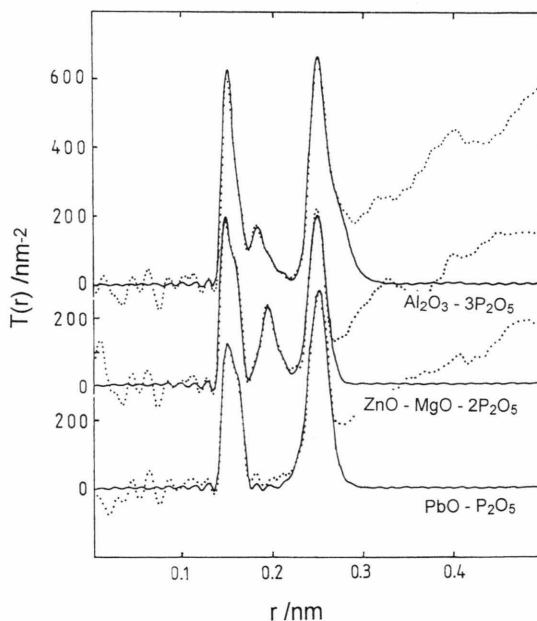


Fig. 3. The functions $T(r)$ in the range up to 0.5 nm. Comparison of the experimental curves (dotted lines) and the model function from the least-squares fits (solid lines). Q_{\max} was chosen to be 420 nm^{-1} .

work, Marquardt's method [17] was used for the least-squares fits of the modified sum of Gaussian curves to the $T(r)$ functions.

Figure 3 presents the distance correlation functions $T(r)$ of the three glasses obtained by Fourier transformations of the $S(Q)$ curves shown in Figure 1. Q_{\max}

was chosen to be 420 nm^{-1} . The resulting partial correlation functions of the atom pairs P–O, Me–O, and O–O (Me stands for the metal atom) are shown in Fig. 4, and Table 1 lists the parameters obtained for the latter curves. For the least-squares fits of the peaks in $T(r)$ two constraints were introduced, namely for the O–O coordination number, which was calculated from $N_{\text{OO}} = 24/(5 + y)$ [9], and for the ratio of the coordination numbers, which was obtained from $N_{\text{P-NBO}}/N_{\text{P-BO}} = (y + 1)/(3 - y)$; where $y = n(\text{Me}_{2/v}\text{O})/n(\text{P}_2\text{O}_5)$ is the molar ratio; and v is the valency of the metal atom.

As can be seen from the peak at about 0.20 nm in the $T(r)$ curve of the glass $\text{MgO-ZnO-2 P}_2\text{O}_5$ (Fig. 3), the partial correlation function of the atom pair Zn–O is completely superimposed on that of Mg–O, i.e. the information content of the experiment is too low to calculate unique coordination parameters from this peak. Therefore, a contrast technique was used that requires the scattering of the sample to be measured with X-rays and neutrons separately in order to obtain two structure factors, $S_X(Q)$ and $S_N(Q)$. Having modified the integrand in (2) by multiplication with the function $M(Q) = \sin(\pi Q/Q_{\text{max}})/(\pi Q/Q_{\text{max}})$, the total distance correlation functions, $T_X(r)$ and $T_N(r)$, are obtained by Fourier transformation. For the ternary glass under discussion, Q_{max} was chosen to be

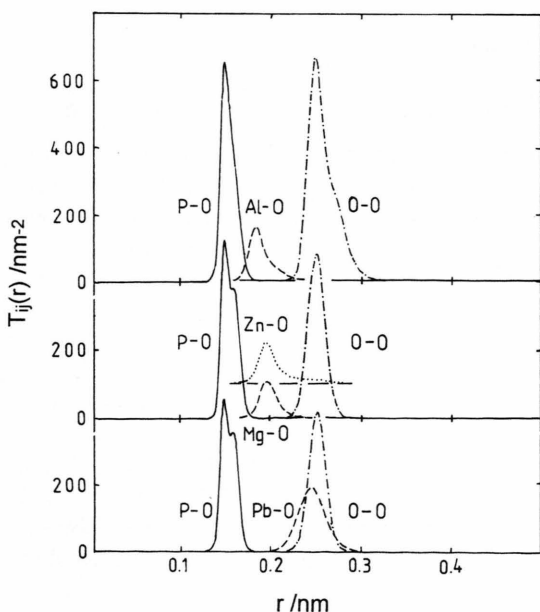


Fig. 4. The partial contributions to the model $T(r)$ functions shown in Figure 3. The curves were calculated using the parameters given in Table 1.

Table 1. Coordination parameters obtained for the metaphosphate glasses studied (On the right hand – coordination numbers and mean values of distances).

Atom pair	Coordination number	Distance (in nm)	fwhm (in nm)	Coordination number	Distance (in nm)
P–O	1.81 (5)	0.148 (1)	0.010 (2)	3.8 (1)	0.154 (1)
	1.99 (5)	0.160 (1)	0.014 (3)		
Zn–O	3.5 (3)	0.195 (2)	0.017 (4)	4.5 (5)	0.198 (2)
	1.0 (2)	0.210 (4)	0.020 (5)		
	1.2 (4)	0.240 (5)	0.05 (1)		
Mg–O	4.6 (3)	0.195 (2)	0.020 (5)	5.5 (5)	0.198 (2)
	0.9 (2)	0.210 (5)	0.020 (5)		
	0.2 (2)	0.240 (8)	0.05 (1)		
O–O	4.05*	0.251 (2)	0.022 (4)		
P–O	2.04 (5)	0.149 (1)	0.011 (2)	4.0 (1)	0.154 (1)
	1.96 (5)	0.159 (1)	0.017 (3)		
Al–O	4.5 (4)	0.183 (2)	0.018 (4)	7.1 (8)	0.189 (2)
	2.6 (4)	0.199 (2)	0.029 (6)		
O–O	3.97*	0.249 (2)	0.019 (4)		
	1.6**	0.268 (4)	0.025 (5)		
	1.0**	0.276 (4)	0.035 (5)		
P–O	1.97 (5)	0.148 (1)	0.010 (2)	3.95 (10)	0.155 (1)
	1.98 (5)	0.160 (1)	0.012 (3)		
Pb–O	1.1 (2)	0.232 (2)	0.025 (3)	5.2 (6)	0.247 (2)
	2.4 (2)	0.248 (2)	0.024 (3)		
	1.7 (2)	0.256 (3)	0.035 (5)		
O–O	2.0*	0.250 (2)	0.018 (3)	4.0*	0.253 (3)
	2.0*	0.256 (2)	0.028 (4)		

* Parameter was fixed; see text.

** The assumption about O–O distances from edges of AlO_6 units was derived from the Al–O coordination parameters

200 nm^{-1} for $S_X(Q)$ and 500 nm^{-1} for $S_N(Q)$. The optimum coordination parameters N_{MeO} and r_{MeO} are thus determined such that the sum-of-squares error resulting from a simultaneous least-squares fit of both $T_X(r)$ and $T_N(r)$ is minimized. Figure 5 demonstrates that the partial correlation function of Zn–O contributes much more to $T_X(r)$ than the function of Mg–O, while their contributions to $T_N(r)$ are of very similar magnitude. The reason is that the scattering power of the Zn and Mg atoms is appreciably different for X-rays but similar for neutrons. This constellation provides the basis for obtaining unique coordination parameters N_{MeO} and r_{MeO} by least-squares fits (Table 1).

To check the reliability of the parameters extracted from the combined evaluation of X-ray and neutron scattering data just described, a definite difference of

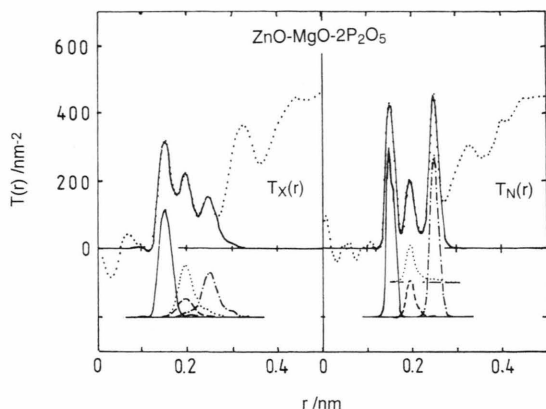


Fig. 5. The functions $T(r)$ of the ZnO–MgO–2P₂O₅ glass obtained by X-ray diffraction, $T_X(r)$, and by neutron scattering, $T_N(r)$. Comparison of experimental curves (dotted lines) and fit results (solid lines). In the lower part of the plot the partial contributions in the notation as used in Fig. 4 are shown.

the two scattering factors experimentally obtained, $S_X(Q)$ and $S_N(Q)$, can be used. The function $\Delta S_{MgO}(Q)$ calculated from the equation

$$\Delta S_{MgO}(Q) - 1 = \frac{[S_X(Q) - 1]b_{Mg}b_0\langle f(Q) \rangle^2 - [S_N(Q) - 1]f_{Mg}(Q)f_0(Q)\langle b \rangle^2}{b_{Mg}b_0\langle f(Q) \rangle^2 - f_{Mg}(Q)f_0(Q)\langle b \rangle^2} \quad (3)$$

contains no correlations of the atom pair Mg–O. Thus, the peak at about 0.20 nm from the $\Delta T_{MgO}(r)$ function (Fig. 6) representing the Fourier transform of $\Delta S_{MgO}(Q)$ can be attributed to Zn–O correlations. (In (3), $f_i(Q)$ is the X-ray scattering amplitude for atom i , and b_i is the neutron scattering length for atom i .) The model distance correlation function (solid line in Fig. 6) was calculated with the parameters given in Table 1 for the P–O, Zn–O, and O–O correlations and appropriate weighting functions $w_{ij}(Q)$,

$$w_{ij}(Q) = \frac{(2 - \delta_{ij})c_i c_j [f_i(Q)f_j(Q)b_{Mg}b_0 - b_i b_j f_{Mg}(Q)f_0(Q)]}{b_{Mg}b_0\langle f(Q) \rangle^2 - f_{Mg}(Q)f_0(Q)\langle b \rangle^2}, \quad (4)$$

where c_i and c_j are the fractions of i and j atoms, and δ_{ij} is the Kronecker symbol. Note, that the O–O partial correlation function has a negativ sign (Fig. 6) due to its negativ weight, $w_{OO}(Q)$. The excellent agreement of the model distance correlation function with the difference function, $\Delta T_{MgO}(r)$, obtained from the diffraction experiments confirms the coordination num-

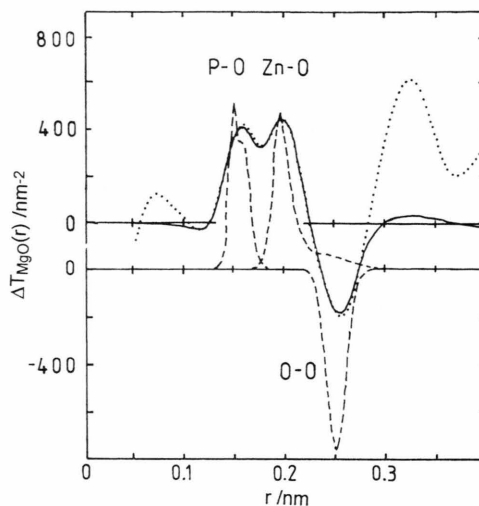


Fig. 6. The experimental function $\Delta T_{MgO}(r)$ (dotted line) is the Fourier transform of the difference of X-ray and neutron structure factors according to (3) containing no Mg–O correlations. The model curve (solid line) is obtained applying the weighting functions given by (4). The partial contributions (dashed lines) shown in the lower part of the plot were calculated using the parameters given in Table 1.

bers and the distances determined for the Zn–O and Mg–O environments.

Discussion

4.1. Modification of the P–O bond character

Two well separated P–O bond lengths in the PO₄ unit found for an NaPO₃ glass [8] (see Table 2) suggest that metaphosphate glasses are suitable objects for a probe of short-range order changes within the network-former unit caused by the network-modifier cations. Considering the results (Figs. 3 and 4) it becomes obvious that the P–O peak splitting is reduced with increasing cation field strength. Note that the upper limits used in the Fourier transformations are of similar magnitude as applied in [8].

The broadening effects of the lines in the Raman spectra [7] and in the ³¹P MAS NMR spectra [6] obtained with increasing Me^{V+} field strength were attributed to the increasing disorder in the glass structure. Thus, a broadening of the Gaussian curves belonging to the two P–O bond contributions is expected. The P–O peak should appear as a broad peak with a less pronounced splitting. But in contrast, the

P–O peaks are found to be very high, which is strongly developed in case of the AlP_3O_9 glass. That gives rise for considerations of effects which are related to changes of the P–O bond character and consequently of the bond lengths.

The field strength of an Me^{V+} ion is proportional to v/r^2 , where r is the ionic radius and v the number of charges. In case of various charges the ratio of Me atoms per PO_4 unit is changed. Thus, the number of NBO's per Me^{V+} ion which is available to form the coordination sphere of metal ions depends on the valency of the Me atom. The Na^+ ion with N_{NaO} equal to about 5 [10] has only two NBO's for itself to form the oxygen sphere. Looking at the related crystal structure [5] it is no surprise that even the BO atoms are involved within the NaO_n polyhedra and the NBO's have two or three sodium cations likewise in the neighbourhood. In the other extrem case it is found that the number of NBO's per Me^{V+} ion is approximately equal to its coordination number, N_{MeO} . In the aluminum polyphosphate crystal [2] all of the NBO's have one Al^{3+} neighbour. Due to both the high positiv charge and the small Al–O distance the highest attractiv forces on the electrons of the NBO's are expected while in case of Na^+ even the BO sites are attached directly.

In Fig. 7 (top) the directions of small shifts of the electron density are shown which are expected for Me^{V+} cations of strong field strength in comparison with the situation found in the NaPO_3 glass. The NBO's are marked by half of an electron charge,

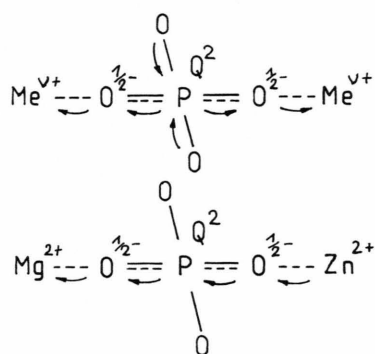


Fig. 7. Illustration of the directions for small shifts of valence electron density via the PO_4 tetrahedron in dependence on the environmental network-modifier cations. In the upper part of the plot, shifts caused from an increasing electric field strength of Me^{V+} ions are shown, and the lower part demonstrates deformations caused from unlike cations on both sides.

which reflects the widely accepted conception [18] of equivalent species of terminal oxygens in the twofold-linked PO_4 units. In accordance to the donor-acceptor approach of Me^{V+} -oxygen interaction, small deformations of the density distribution of the valence electrons are accompanied by changes of bond lengths. Taking into account the rules for changes of lengths due to a shift of electron density along a bond, the following is expected (Gutmann [19]): In consequence of the electron shift from the positively charged P to the negatively charged NBO the distance $r_{\text{P-NBO}}$ becomes greater. Vice versa, in case of BO and P atoms a shortening of $r_{\text{P-BO}}$ is expected. This mechanism explains that with field strength changes from Na^+ to Al^{3+} the splitting of the P–O peak is smeared out and the peak appears much higher (see Figure 1). Pb^{2+} , Zn^{2+} and Mg^{2+} ions play an intermediate role. In the AlP_3O_9 glass, the environment of the PO_4 unit gets a more symmetric character for all of the 4 P–O bonds in comparison with the situation found in the NaPO_3 glass. Hence, the total peak of the P–O distance distribution is narrowed.

The cations of higher field strength produce a weak reduction of the mean P–O distance which is accompanied by a lower O–O distance (see Tables 1 and 2). This effect exceeds slightly the limit of error of our measurements. It confirms the strengthening of the P–O bonds, which is even reflected by the increase of the frequencies of both symmetric Raman bands [7].

The binding energies of the O 1s electrons on the NBO are less changed than on the BO atoms. The values are 531.9 eV for the NBO and 533.7 eV for the BO in NaPO_3 glass [6] but 531.6 eV and 533.1 eV in ZnP_2O_6 glass [20], respectively. This can correspond to the fact that the distance $r_{\text{P-BO}}$ is more shortened than $r_{\text{P-NBO}}$ is lengthened (Tables 1 and 2) though the cations are directly attached to the NBO atoms. It should be noted that the number of NBO's is twice that of BO's. The electron distribution on the BO sites is depleted from both neighbouring phosphorous atoms. Hence, remarkable changes of the P–BO bond must occur.

Table 2. P–O coordination parameters of the sodium metaphosphate glass [8].

Atom pair	Coordination number	Distance (in nm)	Coordination number	Distance (in nm)
P–O	2.1 (1) 2.0 (1)	0.150 0.164	4.1 (2)	0.157

The value of the isotropic chemical shift of the ^{31}P MAS NMR line which is related to the PO_4 middle groups depends linearly on the ionic potential v/r of the Me^{V+} cations [6]. The value of about -47 ppm observed for the AlP_3O_9 glass [11] excellently matches this behaviour. As pointed out in [6], the chemical shift is changed due to the increasing electronegativity of the Me^{V+} ions in the neighbourhood of the oxygen atoms of the PO_4 unit.

4.2. Details of the Al–O environments in the AlP_3O_9 glass

The Al–O coordination parameters in the AlP_3O_9 glass were found [10] to be equal to those in the polyphosphate crystal [2] with N_{AlO} equal to 6. In this case all of the NBO's can form Al–O–P bridges. With respect to the slight deviation from the exact metaphosphate composition in the sample studied, N_{AlO} can be reduced to about 5.9. The charge compensation requires that no NBO's remain without any Al^{3+} neighbour. In accordance to the ^{27}Al MAS NMR results [11], for which the spectra were analyzed on the basis of the satellite transition spectroscopy (SATRAS) [21], a value N_{AlO} of about 5.4 was calculated, taking into account the areas of the peaks attributable to 4-, 5-, and 6-fold coordinated Al^{3+} ions. What are the new details of the Al–O coordination which could be observed by the improved real space resolution?

The present experiment allows to separate the Al–O peak from the P–O peak (Figs. 3 and 4). The mean distance of about 0.189 nm (Table 1) confirms the old result. Obviously, the Al–O distances form an asymmetric distribution which can be approximated by two Gaussian curves in order to find the right shape of the peak. The mean Al–O coordination number is about 7.1 ± 0.8 . Due to the small weight of the Al–O correlation the error of the N_{AlO} value is relatively large. But it must be accepted that on the average more than 6 oxygen atoms are involved in the Al–O environment. Hence, the differences between the results obtained by ^{27}Al MAS NMR and those by diffraction experiments are corroborated. From the NMR it can be concluded that a distribution of different species of AlO_n polyhedra with unlike values N_{AlO} exists [11]. But the NMR does not indicate any 7-fold coordination spheres which consequently leads to a mean N_{AlO} which differs from the diffraction results. Possibly, the ^{27}Al NMR does not perceive oxygen

atoms at distances of about 0.20 nm among other oxygens which are located in contact to the Al^{3+} ion. It is worth mentioning that the broad ^{31}P NMR line corresponding to the twofold linked PO_4 tetrahedra reflects a large variety of local distortions of these units, which in fact indicates the existence of very distorted species of AlO_n polyhedra.

4.3. Zn–O and Mg–O spheres in the ternary systems

By ^{31}P MAS NMR it was found [6] that Zn^{2+} and Mg^{2+} ions in metaphosphate glasses have a similar influence on the isotropic chemical shift. Thus, it seems that both cations produce a similar effect on the PO_4 units. But in binary metaphosphate glasses the values N_{MgO} and r_{MgO} are slightly larger than those found in the Zn–O coordination sphere (see Table 3). What is the result if both cations compete for the electrons located on the PO_4 tetrahedron?

If the distances r_{MgO} and r_{ZnO} are taken from [10] and fixed during the least-squares fit, no satisfactory results were achieved. The best fit is obtained if both Me–O distances are identical with a value of about 0.198 nm. The coordination number N_{MgO} is larger by one than the value N_{ZnO} (Table 1). Such a different behaviour of the coordination numbers was found in the binary glasses as well, but with values (Table 3) lower than the related N_{MeO} values obtained here.

Note that the composition of the ternary system studied slightly deviates from the metaphosphate concentration toward an ultraphosphate glass. For binary ultraphosphate systems it is known [22] that N_{ZnO} and N_{MgO} are continuously increased when the

Table 3. Me–O coordination parameters of binary metaphosphate glasses (methods: X X-ray diffraction, N neutron diffraction).

Atom pair	Coordination number	Distance (in nm)	Method	Reference
Zn–O	4.0 (2)	0.195 (2)	X, N	[10]
	0.5 (2)	0.240 (5)		
Mg–O	4.3 (3)	0.203 (3)	X, N	[10]
	2.0 (5)	0.235 (5)		
Al–O	6.0 (3)	0.189 (3)	X, N	[10]
Pb–O	5.0 (4)	0.2484 (5)	X	[12]
	3.8 (3)	0.3021 (5)		
Pb–O	8.0 (10)	0.247 (5)	EXAFS	[13]
Sr–O	7.0 (5)	0.259 (5)	X	[9]

P_2O_5 content exceeds 50 mol%. Both N_{MeO} values were found to be 6 at 66 mol% P_2O_5 ; which is accompanied by larger Me–O distances. Thus, both facts can be understood, the occurrence of greater values of N_{MeO} and the slight lengthening of the distance r_{ZnO} in comparison with that of the binary systems. But the small r_{MgO} value corresponds to an Mg–O coordination number of about 4, whereas more than 5 oxygen atoms are observed.

For the short Mg–O distance an explanation is required which takes into consideration the specific chemical environment. If one takes into account the electronegativity of the Mg^{2+} ion, which is remarkably higher than that of the Zn^{2+} ion, the electron charge is shifted along a line of bonds via the neighbouring PO_4 unit (see Fig. 7 bottom). In accordance to the rules about changes of bond lengths applied above for P–O bonds [19] it follows that the Zn–O distance must appear increased whereas the Mg–O distance is reduced. Exactly these expectations were confirmed by the experiments. The changes of P–NBO bonds corresponding to this charge transfer cannot be observed because one P–NBO distance of the PO_4 unit should be slightly enlarged whereas the other is reduced. The effect is compensated.

4.4. The asymmetry in the PbO_n polyhedra

The resulting parameters of the Pb–O environment in the PbP_2O_6 glass given in Table 1 are slightly restricted in their reliability due to two points. The nominal composition was used and the contrast of an X-ray measurement in order to separate the O–O and the Pb–O distances could not be applied. The peak area of the O–O distance is calculated using the constraint about N_{OO} value introduced in Section 3.

The Pb–O distance with a value of about 0.247 nm is in agreement with former results (Table 3). For N_{PbO} , the smaller of both values known ($N_{PbO} = 5.0$ [12]) is confirmed. In case of Pb^{2+} ions it is no surprise that low coordination numbers occur, remarkably lower than those observed for the Sr^{2+} ions which are of similar dimension (Table 3). That is attributable to the intermediary character of PbO for the glass formation. The sum of the ionic radii of O^{2-} and Pb^{2+} [23] compared to the Pb–O distance observed indicates a coordination number N_{PbO} smaller than 6. In the lead polyphosphate crystal structure [4] the N_{PbO} is found to be 7.5 but with a broad distribution of Pb–O distances having a mean value of about 0.262 nm. Thus,

the distance and the coordination number in the glass structure are reduced in comparison with the values found in the related crystal.

By use of X-ray diffraction Musinu *et al.* [12] have found further oxygen positions at distances of about 0.30 nm. Note that the Mg–O spheres found in the MgP_2O_6 glass [10] show a similar effect with a remarkable amount of oxygen atoms on more distant positions. From studies on a series of Mg phosphate glasses it was concluded that the 4 NBO's per Me^{2+} at metaphosphate composition are decisive for the formation of the asymmetric MgO_6 octahedra with only 4 oxygens in contact with the Mg^{2+} [22]. This corresponds to the preferred formation of Me–O–P bridges in phosphate glasses as far as this is possible from the energetical point of view. The same mechanism produces in case of Pb^{2+} ions asymmetric environments with on the average 5 oxygens in contact and further 3 more distant oxygen atoms, which is different from the type of PbO_n units found in the crystal [4]. Not all of the 4 NBO's per Pb^{2+} ion can form Pb–O–P bridges. The N_{PbO} value of about 5 at distances of 0.247 nm can be explained by only part of the Pb^{2+} ions being located in PbO_8 units with 4 oxygens in contact and further 4 oxygen atoms at distances of about 0.30 nm. A more detailed description of the different species of PbO_n polyhedra cannot be derived from the mean value of N_{PbO} obtained by diffraction experiments.

A similar effect of asymmetry with two different Na–O distances in the NaO_n polyhedra was observed recently for Na^+ ions in sodium silicate glasses [10]. But different from the MeO_n polyhedra discussed above, the number of NBO's per Na^+ ion is only one, and Na–O–Si bridges do not exist. It was proposed in [10] that these two distances are the result of the formation of non-spherical cavities in the network which must accept the alkali ions. In both mechanisms the more distant oxygens of the distorted MeO_n polyhedra are in contact to neighbouring Me^{V+} ions.

4.5. About the medium-range order

The most pronounced details of the medium-range order of the samples studied are observed in case of the PbP_2O_6 glass. Distinct oscillations in the $Diff(r)$ function (Fig. 2) are found up to distances of about 1.7 nm. The radius of action for structural order is remarkably reduced if not only one, but two different modifier cations (Zn^{2+} and Mg^{2+}) are present in the

glass. For the ternary system, structural details are found up to a distance of only 1.2 nm. The $\text{Diff}(r)$ function for the AlP_3O_9 glass shows a large similarity to that of the SiO_2 glass structure [24] up to r -values of about 1.4 nm. Obviously, the AlO_6 octahedra and other types of AlO_n polyhedra fit very well into the packing of chains formed from linked PO_4 units. Moreover, the edge length of these AlO_6 units is not much greater than the edge length of the PO_4 tetrahedra (Table 1). But it is considered as the most important point that the curvature of meandering chains in the metaphosphate glass is comparable to the curvature of rings in vitreous silica. The diffraction method cannot distinguish between these chains and rings in the medium-range order if the curvature is of comparable magnitude.

5. Conclusions

The investigation of P–O distances within the PO_4 units in metaphosphate glasses by neutron diffraction shows a dependence of the P–O bond lengths on the field strength of the network-modifier cations. Thereby the P–NBO distances are enlarged whereas the P–BO distances are shortened with increasing attractive forces of the Me^{V+} cations toward the negatively charged NBO's. The effect can be attributed to small shifts of electron density within the PO_4 units caused by the electric field of the Me^{V+} cations.

A similar phenomenon was observed when the r_{ZnO} and r_{MgO} values of a ternary phosphate glass

$\text{ZnO-MgO-2P}_2\text{O}_5$ were compared with the Me–O distances found in the related binary glasses. The Mg–O distance is shortened but the distance r_{ZnO} is slightly lengthened in the ternary system. The reason for this effect is attributable to the different attractive forces of both ions against the electron density on the PO_4 units, which are stronger for the Mg^{2+} ion with its higher electronegativity than for the Zn^{2+} ion.

By help of the high resolution of the present experiment, the Al–O coordination number was found to be 7 in the metaphosphate glass, which is slightly larger than that of 6 in the related crystal. Thus, by diffraction methods more oxygen atoms in the Al–O environment can be detected than by ^{27}Al MAS NMR [11]. The Pb–O coordination number in the lead metaphosphate glass is approximately 5, and not 7.5 as found in the corresponding crystal. The short Pb–O distance found for the glass accentuates this behaviour. The formation of very asymmetric PbO_8 polyhedra [12] is comparable with the phenomenon observed for asymmetric MgO_6 octahedra in MgP_2O_6 glasses [10].

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