Structure of $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses studied by x-ray and neutron diffraction

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Abstract

The structures of three $(1-x)\text{GeO}_2\text{-}x\text{P}_2\text{O}_5$ glasses, where $x = 0.02, 0.12$, and 0.19 , have been studied by neutron and x-ray diffraction experiments that yield well resolved P–O and Ge–O bond distances. The Ge–O coordination number (N_{GeO}) increased from 4.0 ± 0.2 to 4.5 ± 0.2 with the increase in x from 0.02 to 0.19 . The increase in N_{GeO} is consistent with a structural model that assumes that all oxygen form Ge–O–Ge and P–O–Ge linkages between Ge-polyhedra and P-tetrahedra and that new GeO_5 or GeO_6 polyhedra are formed with isolated PO_4 units when P_2O_5 is added to GeO_2 . The bond valencies in the P–O bonds of the PO_4 tetrahedra are greater than unity and are balanced in P–O–Ge bridges with underbonded Ge–O links in the GeO_5 or GeO_6 polyhedra. Mixed site connections are expected for the GeO_5 (or GeO_6) and PO_4 units in glasses with relatively low (<20 mole%) P_2O_5 contents due to the overwhelming fraction of GeO_4 tetrahedra. The structural changes are compared with those reported for alkali germanate glasses. Several features indicate different characteristics for the N_{GeO} change of $\text{GeO}_2\text{-P}_2\text{O}_5$ and alkali germanate glasses. However, the distributions of the first-neighbour Ge–O distances are found nearly identical for the $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses and those reported for $\text{K}_2\text{O-GeO}_2$ glasses of equimolar K_2O and P_2O_5 contents.

1. Introduction

The compositional dependence of the molar volume and the refractivity of $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses indicates that the oxygen coordination number of some Ge atoms increases with increasing P_2O_5 content [1]. This phenomenon is similar to that found for alkali germanate glasses, where an increase of N_{GeO} was suggested to explain the anomalous behaviour of several properties [2]. Ge K-edge Extended X-ray Absorption Fine Structure (EXAFS) [3, 4] and Anomalous X-ray Scattering (AXS) [4-6] were used for determination of Ge–O distances and coordination numbers in $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses. The experiments on samples beginning from vitreous (v-) GeO_2 through glasses with ~ 25 mole% P_2O_5 result in an increase of N_{GeO} from 4.0 to 5.6 , and is accompanied by an increase in r_{GeO} distances from ~ 0.175 to ~ 180 nm. The crystal structures [7, 8] of the $\text{GeO}_2\text{-P}_2\text{O}_5$ system show the existence of sixfold coordinated germanium ($^{[6]}\text{Ge}$). This fact demonstrates the possibility of the coexistence of PO_4 and GeO_4 tetrahedra with GeO_6 octahedra to form a germanophosphate network.

The aim of the present work is to investigate the structure of $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses through the use of neutron and x-ray diffraction experiments of high resolving power. Such experiments are possible at neutron spallation sources and at synchrotrons supplying hard x-rays. The resolving power of the AXS experiments in [4-6] was not sufficient to obtain all details of the separate P–O and Ge–O peaks. The focus of the present experiments is the better resolution of the P–O and Ge–O peaks and the determination of the parameters of the corresponding distances with high accuracy. Precise N_{GeO} values are needed for discussion of the underlying structural processes responsible for the coordination changes.

For the alkali germanate ($\text{A}_2\text{O-GeO}_2$) glasses, the absence of non-bridging oxygens (O_{NB}) indicated that

the Ge–O coordination numbers must increase in accordance with the amount of the oxygen introduced by A₂O [9]. Thus, all oxygen atoms should occupy bridging positions (O_B). Diffraction experiments of high resolving power performed on alkali germanate glasses [10, 11] confirmed the increase of N_{GeO} with the additions of A₂O. Analysis of the Ge–O peaks in these studies indicate a fraction of Ge–O distances of ~0.188 nm which are typical of ⁶Ge sites [10, 11].

The addition of P₂O₅, a network-forming oxide, is expected to have different effects on the germanate network than would the addition of network modifying alkali oxides. The structure of glassy (v-)P₂O₅ is formed from PO₄ tetrahedra connected with each other through three corners. The fourth and free corner is occupied by a doubly bonded oxygen (O_{DB}) which is needed to complete the countercharge for compensation of the valency of the P atom [12]. When modifying oxides are added to P₂O₅ glass, the phosphate network disintegrates as non-bridging oxygens form [13, 14] and the 'free corners' of the PO₄ units occupied with O_{DB} participate in the coordination of the modifying cations [14, 15]. The network disintegration ends in the formation of isolated PO₄ units which are connected through four corners to modifying cations.

If the modifier is a network-forming oxide, such as GeO₂, half of an oxygen atom per PO₄ unit is formally transferred to the oxygen polyhedra of the modifier if still isolated PO₄ units are formed which are connected through four corners to modifying cations. Consequently, the mean coordination number of the modifying species increases. Such behaviour is seen for TeO₂-P₂O₅ glasses [16] where TeO₂ is known as a conditional glass former, i.e., the pure component TeO₂ is difficult to obtain in glassy form. The earlier results for the structure of GeO₂-P₂O₅ glasses [3-5] indicate an equivalent increase of N_{GeO} . However, more precise N_{GeO} numbers are needed to confirm the predicted effect of the P₂O₅ added to the glassy germanate networks.

2. Experimental details

Three samples from the GeO₂-P₂O₅ system were prepared with batch compositions of 95, 85 and 75 mole% GeO₂. The glasses were prepared from GeO₂ and NH₄H₂PO₄. Measured amounts of each starting material were ground together in a mortar and pestle, placed into alumina crucibles, and then calcined at 800 °C for 1.5 hours to remove ammonia and water from the system. The samples were then melted at temperatures between 1250 and 1400 °C for 30 minutes before being quenched between copper plates. Compositions were analyzed by taking the average of five points using Energy Dispersive Spectroscopy (EDS). The samples are free of significant Al₂O₃ contaminations (all less than 1 mole%). The three samples have 98, 88 and 81 mole% GeO₂, and are labelled gep98, gep88 and gep81, respectively. The densities of the glasses were measured using Archimedes method with kerosene as the immersion liquid. Measurements were performed on four individual samples of each composition, yielding average densities of 3.587±0.005, 3.577±0.005 and 3.551±0.005 g/cm³ for the three glasses, with increasing P₂O₅ contents. These values convert to atom number densities of 63.1, 68.7 and 72.0 nm⁻³, respectively.

The neutron diffraction experiments were performed at the GEM diffractometer [17] of the spallation source ISIS of the Rutherford Appleton Laboratory (Chilton/UK). The glassy material was crushed and loaded into vanadium cylinders 5.0 mm in diameter and with wall thickness of only 0.025 mm. The beam size was 12 x 40 mm². The duration of the data collection was 5 h for gep98 and >10 h for gep88 and gep81. A 6 mm vanadium rod was used to obtain the incident energy spectrum which is needed for data normalization in the time-of-flight regime. The diffraction data were corrected using standard procedures for container and background scattering, attenuation, multiple scattering and inelasticity effects [18]. The differential scattering cross-sections, dσ/dΩ, collected in detector groups 2 (13°-21°), 3 (24°-45°), 4 (50°-74°), and 5 (79°-106°) were used to compose the final Faber-Ziman structure factors $S_N(Q)$ [19]. Here Q is

the momentum transfer with $Q = 4\pi/\lambda \cdot \sin\theta$ and λ is the radiation wavelength and 2θ is the scattering angle. At first, the data of group 5 were normalized to the total scattering cross-section $\sigma/4\pi$. Subsequently, the data of groups 2, 3, 4 were adjusted to those of group 5. After performing a rough Gaussian fitting of the first-neighbour peaks, the normalization was repeated until agreement of the experimental scattering data with model structure factors calculated with parameters of the Gaussian functions was achieved. Figure 1 shows the weighted experimental $Q \cdot [S(Q) - 1]$ data and the corresponding model functions.

The x-ray diffraction experiments were performed at the BW5 wiggler beamline at the synchrotron DORIS III of Deutsches Elektronen-Synchrotron (Hamburg). An incident photon energy of 122.5 keV ($\lambda = 0.0101$ nm) was chosen for the experiments. The beam size was 1×4 mm². Exact absorption corrections are difficult because the 2.5 mm diameter of the silica capillaries (with wall thickness of 0.01 mm) containing the glassy powder exceeds the beam width. The scattering angles are small ($2\theta = 28^\circ$ for $Q_{\max} = 300$ nm⁻¹) and the transmission coefficients are greater than 0.9 and so the absorption is independent of the angle θ . The electronic energy window of the solid-state Ge-detector was chosen to pass the elastic line and the full Compton peak but not fluorescence radiation. The duration of data collection per sample was 8 h. Dead-time corrections were made with a parameter $\tau = 1.08$ μ s [20] and a fraction of 0.91 of incident photons is polarized horizontally. Corrections were made for background, container scattering, polarization and absorption. Subsequently, scattering intensities were normalized to the structure-independent scattering functions which were obtained from the tabulated atomic elastic scattering factors [21] and atomic Compton scattering data [22]. Empirical corrections with smooth function were used in the range $Q > \sim 220$ nm⁻¹ to make the scattering intensity oscillate around the structure-independent scattering. Deficits in the calculation of the Compton fraction, uncertainties with the chemical compositions, errors in the instrument calibration, instabilities of beam position and of monitor efficiencies can cause the deviations. Finally, the Faber-Ziman structure factors, $S_x(Q)$, are calculated [19, 23].

3. Results

3.1. Structure factors and correlation functions

The neutron and x-ray structure factors shown in figures 1(a),(b) are weighted with Q to make visible the oscillations in the high- Q range. The neutron data for $Q > 360$ nm⁻¹ are scattered and the corresponding model $Q \cdot [S(Q) - 1]$ functions of the samples gep88 and gep81 are very flat in this range. An increase in the data acquisition time would have only little improvement on the resolution in this region. The x-ray data of gep88 show unphysical differences with the model function at Q of ~ 280 nm⁻¹.

Since the data of high Q -values are noisy, Fourier transformations (FT) are performed with damping of $S(Q)$ using $Q_{\max}$ of 500 and 318 nm⁻¹ for neutrons and x-rays, respectively. The real-space correlation functions, $T(r)$, are obtained with

$$T(r) = 4\pi r \rho_0 + 2/\pi \int_0^{Q_{\max}} Q \cdot [S(Q) - 1] M(Q) \sin(Qr) dQ \quad (1)$$

where ρ_0 is the number density of atoms and the damping function $M(Q)$ used is $M(Q) = \sin(\pi Q/Q_{\max})/(\pi Q/Q_{\max})$ [24]. The resulting $T(r)$ functions are shown in figure 2. Since the data ranges with high Q -values are very important to resolve the details of the narrow peaks of covalent bonds the FT procedures are also repeated without damping and with $Q_{\max}$ values of 360 and 318 nm⁻¹ for the neutron and x-ray data, respectively. The corresponding $T(r)$ functions without damping are shown in figure 3. The P–O and Ge–O first-neighbour distances are resolved for gep88 and gep81, and are better without damping as shown in figure 3. The fraction of P₂O₅ in gep98 is too small to show significant P–O correlations. The $T(r)$ functions of gep81 plotted in figure 3 (no damping) show clear shoulders at ~ 0.195 nm

which could be interpreted as the contributions from GeO₆ octahedra possessing greater Ge–O distances, however, peaks at this distance are also found for the other two samples. The peaks are due to satellite ripples caused by the termination effects from FT according to equation (1) and the shoulder of the Ge–O peak of gep81 appears enhanced from the termination effect. Therefore, P–O and Ge–O peaks shown in figure 2 exhibit more realistic shapes without the FT termination ripples but the damping causes some peak broadening. The position of the Ge–O peak shifts by 0.002 nm to greater distances in the series gep98 < gep88 < gep81. In addition, there is an increasing asymmetry of the peaks for gep88 and gep81, whereas the peak of gep98 is still nearly symmetric. A separate component at ~0.188 nm which could be related to ^[6]Ge sites, is not found in the Ge–O peaks.

3.2. Gaussian fitting of the first-neighbour peaks

The height of the P–O peak at a bond length of ~0.155 nm grows continuously with P₂O₅ content. P–O–P bridges are not expected for the glasses with low P₂O₅ contents [13, 14]. A variety of lengths of P–O bonds in P–O–Ge bridges can arise from links with the different GeO₄, GeO₅ and GeO₆ units. Nevertheless, the fit of the P–O peak is successful with a single Gaussian function. In the case of gep98, the parameters of the model P–O peak are fixed because the peak area is very small. The Ge–O peak at ~0.175 nm is accompanied by a tail extending to 0.21 nm (figures 2, 3). Two Gaussian functions are used to fit the Ge–O peak to account for this asymmetry. The parameters of the Gaussian functions are the coordination numbers, N_{ij} , the mean distances, r_{ij} , and the peak widths (full widths at half maximum), Δr_{ij} , for the pairs of atomic species i and j . Gaussian fitting is performed to the $T_N(r)$ and $T_X(r)$ data simultaneously. The effects of termination of the FT integral at $Q_{\max}$ are taken into account by convolution of the Gaussian peaks with functions $P_{ij}(r)$ [25, 26]. This procedure simulates the Q -window and damping used in equation (1). In case of x-ray scattering, different dependencies on Q of the weighting factors $w_{ij}(Q)$ cause specific features. For example, flat tails occur on both sides of the Ge–O peaks, extending to 0.13 nm or to 0.24 nm. These effects are reproduced in the model functions by appropriate use of the convolution method mentioned above. Least-squares fits using the Marquardt algorithm [27] are only performed to the $T(r)$ functions obtained with damping (figure 2). Small differences at ~0.195 nm exist for the model functions of gep88 and gep81 shown in figure 2(a). The resulting peak parameters are listed in table 1. Subsequently, for the $T(r)$ data obtained without damping (figure 3), model functions are calculated by use of these parameters. Here, good agreement is found with even the termination ripples well reproduced. Only in the case of the x-ray data of gep88 do some differences exist at lengths of ~0.12 nm. These differences may be caused by the unphysical features at ~280 nm⁻¹ observed in the $Q[S(Q)-1]$ function of gep88 (figure 1(b)).

The total Ge–O coordination numbers and the corresponding mean distances given in table 1 indicate the formation of ^[5]Ge or ^[6]Ge sites as the P₂O₅ content is increased. The P–O coordination numbers obtained for all samples are four, within the limits of error. The P–O peaks are narrow and well fitted with a single Gaussian function, as was found for the P–O peaks obtained for TeO₂-P₂O₅ glasses [16].

Some peaks of the O–O, Ge–P, and Ge–Ge correlations are added to the model functions using reasonable peak parameters which are empirically optimized. For example, the O–O peak at ~0.251 nm, caused by the edges of PO₄ tetrahedra, is needed to correctly simulate the right flank of the Ge–O peak. This O–O contribution increases with increasing P₂O₅ content, whereas that at ~0.285 nm decreases. The latter distance is due to the edges of the GeO₄ tetrahedra (see figure 3(a)). As P₂O₅ is added, the height of the peak at 0.285 nm decreases to less than that of the peak at 0.251 nm although the number of Ge atoms is still greater than that of P atoms. This fact is a further indication for a change in the coordination

of the GeO₄ units. With increasing P₂O₅ content, additional O–O distances occur at ~0.265 nm. Such lengths can be attributed to the edges of GeO₆ octahedra. In principle, a quantitative analysis of the O–O correlations of the neutron $T(r)$ function could help to determine the fractions of the different GeO_{*n*} groups, but the edge lengths of possible GeO₅ polyhedra are not known. Secondly, we do not know the widths of the overlapping O–O correlations of the PO₄ units and the different GeO_{*n*} polyhedra. The edge lengths and peak widths of these correlations can change with glass composition. In the x-ray $T(r)$ functions the O–O correlations possess little weight but the Ge–P and Ge–Ge correlations dominate. The P–P peak caused by P–O–P links would appear at ~0.295 nm, but indications for such linkages in significant numbers are not found.

4. Discussion

4.1. Compositional dependence of the Ge–O coordination number

The Ge–O coordination numbers for the (1–*x*)GeO₂–*x*P₂O₅ glasses obtained in two independent diffraction experiments possess greater accuracy than the N_{GeO} numbers obtained by AXS [4–6]. The continuous change of N_{GeO} from 4.0±0.2 to 4.3±0.2 and 4.5±0.2 with increasing *x* is small but significant. These numbers can be compared with the behaviour predicted in section 1, where isolated PO₄ units which are connected through four corners provide additional oxygens to form P–O–Ge bridges to GeO_{*n*} units with *n* > 4. The corresponding structural changes are expressed for GeO₅ units by the relationship [16]

where O_{1/2} represents a bridging oxygen atom (P–O–P, Ge–O–Ge, or Ge–O–P). Some GeO_{4/2} units of v-GeO₂ are converted to Ge-units with greater coordination numbers (N_{GeO}) and these new germanate sites are charge-balanced by the formation of isolated PO_{4/2} units from P₂O₅.

Figure 4 shows the dependence of N_{GeO} on composition for the P₂O₅ containing glasses and for Na₂O- and K₂O-containing germanate glasses [10, 11]. The glass compositions are represented by the mole fractions $\alpha(\text{M}_z\text{O})$ for the M_{*a*}O_{*b*} oxides, where $z = a/b$. From equation (2), the effect of composition on N_{GeO} is described by

$$N_{\text{GeO}} = 4 + 0.4 \alpha(\text{P}_{0.4}\text{O})/\alpha(\text{GeO}_2) \quad (3)$$

where $\alpha(\text{GeO}_2)$ is the corresponding mole fraction for GeO₂. Equation (3) is represented by the dotted line labelled 'model D' in figure 4, as described in an earlier study of the structures of (1–*x*)TeO₂–*x*P₂O₅ glasses [16]. The present N_{GeO} results match the predicted behaviour very well. The N_{GeO} of two germanophosphate crystal structures [7, 8], where all oxygen atoms are in bridging positions, are found on the corresponding 'model D' line, as well. The AXS results [4–6] follow the 'model D' predictions only roughly. Structural deviations from 'model D' might be due, for example, to some O atoms that have three Ge neighbours (e.g. as in the rutile form of GeO₂ [29] or in Na₄Ge₉O₂₀ [30]), giving a value of N_{GeO} greater than predicted. In germanate crystals with second oxides such as the conditional glass formers Al₂O₃ or ZrO₂ [31, 32], the Ge atoms form only GeO₄ tetrahedra. Glasses of the GeO₂–TeO₂ system have been studied by EXAFS, where the formation of some GeO₆ octahedra was reported [33].

An increase of N_{GeO} is well known for the alkali germanates. Figure 4 shows the N_{GeO} of four crystal structures. The first of them (Na₄Ge₉O₂₀ [30]) possesses some oxygens with three ⁶Ge neighbours. The N_{GeO} values of A₂O–GeO₂ glasses obtained by neutron diffraction of high resolving power [10, 11] are comparable to those indicated by the other three crystal structures [34–36]. Up to compositions with $\alpha(\text{A}_2\text{O}) \sim 0.2$, all oxygens form Ge–O–Ge bridges, as noted in section 1. The structural changes have been summarized by [37]

and the corresponding increase of N_{GeO} is given by 'model E' with

$$N_{\text{GeO}} = 4 + 2 c(\text{A}_2\text{O})/c(\text{GeO}_2) . \quad (5)$$

The octahedral GeO₆ units result from sp³d² hybridization and figure 5(a) shows a representation of its bonding environment. The N_{GeO} of the alkali germanate glasses follows compositional 'model E' up to modifier additions of ~0.2. With additional modifier, the germanate structure returns to that based on GeO₄ units and the formation of non-bridging oxygens becomes significant. A corresponding maximum limit in N_{GeO} is not indicated for the GeO₂-P₂O₅ glasses studied to date [4, 5, this work] or for the related crystals [7, 8].

The effect of composition on N_{GeO} for the GeO₂-P₂O₅ glasses is similar to that found for the compositional dependencies of N_{TeO} for TeO₂-P₂O₅ glasses [16]. In both cases, the reasons for these changes are attributable to properties of the PO₄ units [13-15]. In contrast, when alkali oxides are added to the germanate and tellurite networks, the N_{GeO} and N_{TeO} values have different compositional dependencies, as expressed by 'model E' for the germanates and 'model A' (see [16]) for the tellurites. In 'model A', the addition of A₂O reduces N_{TeO} as TeO₄ units are replaced by TeO₃ units.

For alkali additions to GeO₂, the increase of N_{GeO} prevents formation of O_{NB} but it supplies suitable O_B sites for more uniform distributions of the negative charge needed to surround the A⁺ ions. In tellurite glasses, alkali additions create O_{NB} such as in silicate networks, but the number of O_{NB} is doubled by the TeO₄ → TeO₃ transition, which increases the number of suitable O_{NB} sites for more uniform distributions of the negative charge needed to surround the A⁺ ions. In the case of the P₂O₅ additions the N_{GeO} (or N_{TeO}) increases. The germanate (or tellurite) part of network accommodates that half oxygen atom which is provided by the change from a PO_{3/2}O to a PO_{4/2} unit (equation (2)). The formation of regular PO_{4/2} tetrahedra, this is the optimum tetrahedral conformation, becomes possible with equivalent linkages through its four corners to GeO_n (or TeO_n) units.

4.2. Distributions of the P–O and Ge–O bond lengths

The change of N_{GeO} results directly from the experimental data. Equation (2) gives an explanation of this behaviour with the change of groups for the case of a GeO₄ → GeO₅ transition. An analogous relationship could be given for the formation of the GeO₆ units. But knowledge of the preference of either the ^[6]Ge or ^[5]Ge sites is not available. Clarification is also desired for details of the linkages between the different groups. The P and ^[5]Ge (and/or ^[6]Ge) sites are neighbours through P–O–Ge linkages for reasons of charge balance. But each of the P and ^[5]Ge (and/or ^[6]Ge) sites should have GeO₄ neighbours, as well, because the greatest fraction of Ge in the glasses studied is that of the ^[4]Ge sites.

The distributions of bonds in the structures of the Ge₅O(PO₄)₆ [7] and GeP₂O₇ [8] crystals show that the PO₄ tetrahedra possess three ^[6]Ge neighbours but also a ^[4]Ge or P neighbour, respectively (see figure 5(b),(c)). The bond lengths in the PO₄ units are different in linkages with octahedra or tetrahedra while the ^[6]Ge form regular octahedra. A structure formed of only PO₄ and GeO₅ (figure 5(d)) is possible (33 mole% P₂O₅) where the P–O bonds of the PO₄ are in equal linkages with four ^[5]Ge. GeO₅ polyhedra possess less regular shapes with geometries ranging from square pyramids to trigonal bipyramids. But uniform environments with equal groups in the neighbouring positions are probably rare for the PO₄ or GeO₆ units existing in the glass structures with the chemical compositions used in this work.

The P–O peaks of the samples gep88 and gep81 have been approximated with single Gaussian functions. The peak widths are similar to those obtained earlier [28, 38] for either the peaks of the P–O_T or P–O_B bonds. The terminal oxygens (O_T) include the O_{DB} known from the PO_{3/2}O units and the O_{NB} created by breakage of P–O–P bridges using the oxygen of the modifier oxide. The O_{DB} and O_{NB} cannot be

differentiated in the PO₄ tetrahedra [14]. The position of the P–O peak at ~0.153 nm (table 1) is of the same magnitude as the mean bond lengths found for other binary phosphate glasses [28, 38].

The 'isolated' PO₄ tetrahedra in the crystal structure of Ge₅O(PO₄)₆ [7] (figure 5(c)) have different lengths of P–O bonds in bridges with either the ^[6]Ge or ^[4]Ge sites with ~0.150 or 0.159 nm, respectively. Observation of split P–O peaks such as found for the P–O_T and P–O_B bonds of other binary phosphate glasses [28, 38] is not possible with such distances and Q_{max} of only 360 nm⁻¹. But the differences of bond lengths would increase the width of the P–O peak significantly. Due to the change of contrast of the P–O and Ge–O correlations in the x-ray and neutron diffraction data (figures 3(a),(b)) inappropriate separations of the first-neighbour peaks would become visible but the fits were successful with single and narrow P–O peaks.

The situation in the germanophosphate glasses with the compositions used in this study is expected to differ from that in the Ge₅O(PO₄)₆ crystal [7] where ^[4]Ge–O–^[6]Ge bridges do not exist and, consequently, an optimum exchange of charges with the PO₄ tetrahedra is not possible. In the glasses with greater numbers of GeO₄ units coexisting with the P and ^[5]Ge (and/or ^[6]Ge) neighbours all the latter sites should possess some GeO₄ neighbours and a GeO₄ unit should form linkages with unlike groups, as well. The balance of bonding forces is accompanied with shifts of charges across the different groups which reduces the differences between the lengths of P–O bonds in the P–O–^[n]Ge linkages with $n = 4, 5, 6$ as shown in figure 6. According to equation (2) two PO₄ tetrahedra provide the GeO₆ unit with two additional electrons. This consideration implies that the single P–O bonds in the bridges with the ^[6]Ge and ^[4]Ge sites should possess lengths close to those known of P–O_B bonds (~0.160 nm [28, 38]). However, due to the high positive charge at the P⁵⁺ ion, part of the negative charge formally given to the GeO₆ retains closer to the P⁵⁺. In the circuit shown in figure 6(b) the charge shifts two ways, the direct way and that across the ^[4]Ge site. The Ge–O bonds of the GeO₆ appear underbonded and the P–O bonds become overbonded irrespective of the kind of neighbouring GeO_n group. Thus, the small width of the P–O peak should not be used as an indication for links with equal ^[n]Ge sites of a definite n . The bonds in the GeO₄ unit change differently: those in competition with the P sites (P–O–^[4]Ge linkages) are elongated while those in ^[4]Ge–O–^[6]Ge linkages are shortened.

Despite the differences existing between the Ge–O coordination change of GeO₂-P₂O₅ and A₂O-GeO₂ glasses, it is worthwhile to compare the Ge–O results shown in table 1 with the parameters of the Ge–O distance peaks reported for K₂O-GeO₂ glasses [11, 39]. An N_{GeO} of ~4.3 and a mean Ge–O distance of 0.178 nm with the first sharp component at 0.175 nm were found for the K₂O-GeO₂ sample of 11 mole% K₂O [11, 39]; virtually identical structural parameters were obtained for gep88 (table 1). An N_{GeO} of ~4.3 (neutron data [11]) or ~4.5 (x-ray data [39]) and a mean distance of 0.180 nm with the first sharp component at 0.1755 nm are reported for the 20 mole% K₂O glass and the same values were obtained for gep81. The first components are more narrow for the K₂O-GeO₂ glasses.

The comparisons of the lengths of the Ge–O bonds and the relationships (2) and (4) suggest to assume similar effects of (PO_{4/2})⁺ groups and K⁺ ions if they are incorporated in germanate networks (with K₂O fractions less than 20 mole%). Figure 7 shows that both ions can occupy equivalent sites, as an example, here in interaction with a GeO₅ and two GeO₄ units. Above we discussed partial shift of negative charge from the ^[5]Ge site to the O atoms which leads to underbonded Ge–O bonds in the GeO₅ unit but overbonded P–O bonds. Underbonded Ge–O bonds in the GeO₅ unit of the K₂O-GeO₂ glass (figure 7(b)) are balanced by the K⁺ ions. The negative charge of the GeO₅ unit is located at those oxygen sites which approach the K⁺. The two oxygens share the character of an O_B with that of an O_{NB}. This view is overly

simple and the exact distribution of charges is more complicated. For example, the third oxygen neighbour of the K⁺ ion shown in figure 7(b) should carry more negative charge than that in a simple ^[4]Ge–O–^[4]Ge bridge. The analogy of K⁺ ions and (PO_{4/2})⁺ groups ends for glasses with K₂O contents of ~20 mole% [10], when non-bridging oxygens form and N_{GeO} decreases to four for K₂O-GeO₂ glasses.

5. Conclusions

The mean Ge–O coordination numbers, N_{GeO} , of GeO₂-P₂O₅ glasses increase with P₂O₅ additions in accordance with the assumption that all oxygen atoms are found in Ge–O–Ge or P–O–Ge bridges for the glasses studied here, with P₂O₅ contents up to 19 mole%. New GeO₆ or GeO₅ polyhedra are formed, coexisting with GeO₄ and isolated PO₄ units, as P₂O₅ is added to the GeO₂ glass. The bond valencies in the P–O bonds are greater than unity and are balanced in P–O–Ge bridges with underbonded Ge–O links from GeO₅ or GeO₆ polyhedra. Mixed site environments are expected for the GeO₅ (or GeO₆) and PO₄ units in glasses with lower P₂O₅ contents due to the greater fraction of the GeO₄ tetrahedra. Despite the different groups which are connected with the PO₄ tetrahedron the peaks of P–O distances are narrow. This behaviour implies that all P–O bonds in the linkages P–O–^[n]Ge with $n = 4, 5, 6$ are nearly identical and overbonded. The distributions of the first-neighbour Ge–O distances are found to be nearly identical for the GeO₂-P₂O₅ glasses and those reported for K₂O-GeO₂ glasses of equimolar K₂O and P₂O₅ contents. This is explained by assuming that the electron as countercharge of a given K⁺ ion is almost distributed at the adjacent bridging oxygen sites and does not participate in the covalent Ge–O bonds.

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Table 1. Parameters resulting from Gaussian fitting of the P–O and Ge–O first-neighbour peaks of the three GeO₂-P₂O₅ glasses. Numbers in parenthesis give the uncertainty in the last digit. The parameters of the O–O peak are fixed for all samples.

Sample label	Atom pair	Peak parameters			Ge–O coordination number	Mean Ge–O distance (nm)
		N_{ij}	r_{ij} (nm)	Δr_{ij} (nm)		
gep98	P–O	4.00 ^a	0.153 ^a	0.010 ^a		
	Ge–O	3.65	0.1742	0.011	4.00(20)	0.175(1)
		0.35	0.188	0.020 ^a		
		0.50 ^a	0.252 ^a	0.020 ^a		
	O–O	0.50 ^a	0.265 ^a	0.025 ^a		
		5.00 ^a	0.285 ^a	0.025 ^a		
gep88	P–O	4.3(5)	0.153(2)	0.011(2)		
	Ge–O	3.28	0.1747	0.012	4.28(20)	0.178(1)
		1.00	0.188	0.024		
		1.70 ^a	0.251 ^a	0.019 ^a		
	O–O	1.20 ^a	0.265 ^a	0.025 ^a		
		1.60 ^a	0.265 ^a	0.025 ^a		
gep81	P–O	4.14(20)	0.153(1)	0.009(2)		
	Ge–O	3.07	0.1755	0.014	4.51(20)	0.180(1)
		1.44	0.188	0.021		
		2.40 ^a	0.251 ^a	0.019 ^a		
	O–O	2.00 ^a	0.265 ^a	0.025 ^a		
		2.30 ^a	0.286 ^a	0.022 ^a		

^a These values have been fixed in the fits.

Figure 1. Weighted interference functions of the three samples studied: (a) neutron data and (b) x-ray data. The experimental data (dots) are compared with model functions (lines) which are calculated with the parameters of peaks used for the model $T(r)$ functions shown in figures 2 and 3. Upper functions are shifted for clarity.

Figure 2. Correlation functions in the range of the first-neighbour peaks of the $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses (dotted lines): (a) neutron and (b) x-ray data obtained with damping in FT and Q_{max} of 500 and 318 nm^{-1} . The model $T(r)$ functions are given as thick solid lines where reasonable parameters for the O–O, Ge–P and Ge–Ge peaks are chosen arbitrarily without fits. The model P–O (thin solid lines) and Ge–O (dashed lines) components obtained by peak fitting are shown as separate peaks. Upper functions are shifted for clarity.

Figure 3. Correlation functions in the range of the first-neighbour peaks of the $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses (dotted lines): (a) neutron and (b) x-ray data obtained without damping in FT and Q_{max} of 360 and 318 nm^{-1} . The model $T(r)$ functions calculated with the peak parameters already used in figure 2 are given as thick solid lines. The model P–O (thin solid lines) and Ge–O (dashed lines) components are also shown separately. Definite O–O distances are marked by arrows and are related to edge lengths of the structural groups indicated in the plot. Upper functions are shifted for clarity.

Figure 4. Compositional behaviour of the Ge–O coordination numbers of the $\text{GeO}_2\text{-P}_2\text{O}_5$ glasses studied, of N_{GeO} values obtained by AXS [4, 5] and of N_{GeO} values of alkali germanate glasses with Na_2O [10] and K_2O [11] versus contents of the second component. The N_{GeO} numbers are compared with those of some related crystal structures ($\text{Ge}_5\text{O}(\text{PO}_4)_6$ [7], GeP_2O_7 [8], $\text{Na}_4\text{Ge}_9\text{O}_{20}$ [30], $\text{Na}_2\text{Ge}_4\text{O}_9$ [34], $\text{Li}_2\text{Ge}_2\text{O}_5$ [35], Li_2GeO_3 [36], $\text{Al}_2\text{Ge}_2\text{O}_7$ [31], ZrGeO_4 [32]). The dashed, dotted and solid lines specify the behaviour of N_{GeO} according to three compositional models (C, D, and E, respectively) originally developed to understand N_{TeO} behaviour in binary tellurite glasses [16]. The models are described in the text.

Figure 5. Schemes of germanate networks: (a) linkages to a GeO_6 octahedron in an alkali germanate; (b) linkages between P and Ge units in the GeP_2O_7 crystal [8]; (c) linkages between P and Ge units in the $\text{Ge}_5\text{O}(\text{PO}_4)_6$ crystal [7]; (d) possible linkages between P and Ge units in a structure with 33 mole% P_2O_5 . The numbers indicated in the plots are bond lengths given in picometres. Oxygen atoms have been removed for clarity.

Figure 6. Network sections showing the linkages between the PO_4 , GeO_6 , and GeO_4 groups (a) as arranged in the $\text{Ge}_5\text{O}(\text{PO}_4)_6$ crystal [7]; (b) as suggested for glasses of P_2O_5 contents less than 20 mole%. Arrows indicate the directions of partial shifts of electron charges.

Figure 7. Network sections with a) PO_4 and, b) K^+ sites inserted into the germanate structures showing the analogous effect of their incorporation in germanate networks here with adjacent GeO_5 and GeO_4 groups. P_2O_5 and K_2O contents are less than 0.2.