The Structure of Gallium Phosphate Glasses by High-energy X-ray Diffraction

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X-ray diffraction experiments are used to obtain short-range order information of gallium phosphate glasses of meta- and pyrophosphate compositions. Parameters of the first-neighbor peaks, such as coordination numbers and distances, are obtained. A strong decrease of the Ga-O coordination number from 6.0±0.2 to 4.6±0.2 upon Ga_2O_3 addition is found, which is accompanied by a shortening of the Ga-O distances. Only GaO_6 octahedra exist at the metaphosphate composition. Close to the pyrophosphate composition, the majority of Ga atoms occupies already tetrahedral sites. The Ga-O coordination number behaves equivalent with the ratio $M_{TO} = n(O_T)/n(Ga)$, thus, with the number $n(O_T)$ of terminal oxygen atoms (O_T) in phosphorus-O_T bonds which are available for the coordination of each Ga atom. Thus, P-O_T-Ga bridges are formed for all O_T atoms. The GaO_n polyhedra neither share O_T atoms nor form Ga-O-Ga bridges. With increasing fraction of GaO_4 tetrahedra and decreasing lengths of the phosphate chains the network expands.

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

1. Introduction

The oxides of gallium and phosphorus, Ga_2O_3 and P_2O_5, are known as network-forming materials [1] where GaO_4 and PO_4 tetrahedra are the basic structural units. The two oxides can complement each other. Phosphorus can donate electron charge to gallium which would stabilize tetrahedral environments of both atoms. This mechanism is well developed in $GaPO_4$ crystals [2, 3] where equal fractions of oxides are mixed and structures similar to silica polymorphs are formed.

The glass-forming range of the Ga_2O_3-P_2O_5 system is, however, limited to compositions rich in P_2O_5 [4]. Following the rules of network changes for phosphate glasses [5] addition of modifying oxide leads to the disruption of P-O-P bridges where, at first, three-connected PO_4 branching units are transformed to two-connected middle units before single-connected PO_4 end units or, in the end, isolated PO_4 units occur. At metaphosphate composition, i. e. in glasses of 25 mole% Me_2O_3 (with the more general formula $Me_{1/v}PO_3$, where v is the valency of Me), chain and/or ring structures of PO_4 middle groups are formed. With further modifier addition the chains become shorter and at the pyrophosphate composition, i. e. in glasses of 40 mole% Me_2O_3 (with the more general formula $Me_{4/v}P_2O_7$) the PO_4 dimers dominate. The corresponding changes are widely proved by results of ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) and vibrational spectroscopy. Many of such results are reviewed in [6].

The only known crystal structure in the range of glass formation with Ga atoms as the third species is that of $Ga(PO_3)_3$ polyphosphate [7], where infinitely long, meandering phosphate chains are interconnected via GaO_6 octahedra. A similar structure is also known of an $Al(PO_3)_3$ modification [8]. Another detail of these structures is the fact that all oxygen atoms are either in P-O-P or P-O-Ga(Al) bridges where, consequently, the GaO_6 (AlO_6) octahedra

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don't share any oxygen. Obviously, it is profitable for terminal P-O$_T$ bonds (O$_T$ = terminal oxygen) to share the double-bond character and to coordinate a second atomic neighbor. This principle requires a six-fold coordination of Ga(Al) atoms which is not common of Ga(Al) atoms in gallate(aluminate) glasses. Except of the P_2O_5 polymorphs, no phosphate crystal is known which would possess 'dangling' P-O$_T$ bonds [9]. Obviously, P-O$_T$ bonds without a second neighbor of O$_T$ are reactive and, thus, are avoided. From this finding the same behavior was concluded to exist in phosphate glasses. This trend, and also the attempt to stabilize Me-O$_T$-P bridging positions in symmetric MeO$_n$ environments were used to explain the density anomalies in phosphate glasses of bivalent modifier (Me) atoms [10, 11].

Rare earth oxides cause similar effects in binary phosphate glasses [12 - 14], which could be studied extensively only after applying a melt technique which avoids loss of the volatile P_2O_5 component at the required high melting temperatures. The same problem limits the sample preparation also for Ga phosphate glasses, where the batches for ultraphosphate samples which were melted in open crucibles result in metaphosphate glasses [15]. On the side of high Ga_2O_3 fractions, Ga phosphate glasses are obtained up to the pyrophosphate composition [4, 15]. Changes of the PO_4 units in the corresponding glasses were analysed by vibrational spectroscopy [15], where also comparisons with the $Ga(PO_3)_3$ crystal were made. If compared with Al phosphate glasses [16], the larger range of glass formation makes the Ga_2O_3-P_2O_5 system more suitable to study structural changes in modifier environments. Ga atoms are good scatterers of X-rays. Ga-O bonds are longer than Al-O bonds, and thus are well resolved from P-O correlations. So X-ray diffraction experiments using high-energy photons are excellent in a search for changes in Ga-O environments. Though Al phosphate glasses were prepared [16] only in a small range with molar fractions, x, of Al_2O_3 within $0.31 < x < 0.35$, significant changes of the Al environments were detected by ^{27}Al MAS NMR. With increasing x the fraction of AlO_4 tetrahedra increases at the expense of AlO_6 octahedra, whereby the clear fraction of AlO_5 units is about constant. In this work X-ray diffraction experiments are made to extract the short-range order information of Ga_2O_3-P_2O_5 glasses in the range $0.25 \le x \le 0.40$, where the same sample material as prepared and studied in [15] is used.

2. Experimental

2.1. Sample Preparation

Details of the sample preparation are described in [15]. Batches of Ga_2O_3 and $NH_4H_2PO_4$ were heated at 400°C and then melted in Pt crucibles for 20 min at 1300 - 1550 °C. Electron probe microanalysis revealed that, starting with batches containing $0.15 \le x \le 0.30$ mole fractions of Ga_2O_3, glass samples close to metaphosphate composition (x = 0.25) were obtained, while batches of 0.35 and 0.40 mole fractions Ga_2O_3 yielded samples close to pyrophosphate composition (x = 0.40). IR and Raman spectra confirmed that all glasses could be devided into the two groups [15]. One sample of each group was chosen for the X-ray diffraction experiments. After first Gaussian fitting using x = 0.25 and 0.40 for the two samples, compositions have been changed to x = 0.27 and 0.38 (cf. Chapter 3).

2.2. Diffraction Experiments

The X-ray diffraction experiments were performed at the BW5 wiggler beamline at DORIS III of Deutsches Elektronen-Synchrotron (Hamburg). An incident photon energy of 120 keV (λ = 0.0104 nm) was chosen for the experiments. The beam size was 1×4 mm^2. Since the diameters of 2.5 mm of the silica capillaries (with wall thicknesses of 0.01 mm) containing the glassy powder are larger than the beam width exact absorption corrections are difficult. The scattering angles are small ($2\theta = 28°$ for $Q_{\max}$ = 300 nm^{-1}) and the transmission coefficients are higher than 0.9, so that absorption is independent of the scattering angle. Q is the magnitude of a scattering vector with $Q = 4\pi/\lambda \sin\theta$. The electronic energy window of the solid-state Ge-detector was chosen to pass the elastic line and the full Compton peak but no fluorescence radiation. Dead-time corrections are made [17] with the parameter θ = 1.08 µs. A fraction of 0.91 of the incident photons is polarized horizontally. Corrections are made for background, container scattering, polarization and absorption. The scattering intensities are normalized to the structure-independent scattering functions which are calculated by a polynomial approach [18] of tabulated atomic data of the elastic scattering factors [19]. Compton scattering is calculated according to [20]. Finally, the Compton fraction is subtracted and the Faber-Ziman structure factors, $S(Q)$, are obtained [21, 22].

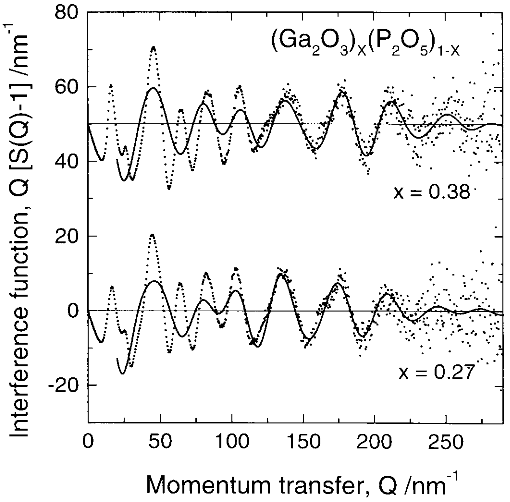


Fig. 1. Weighted interference functions, $Q[S(Q)-1]$, of the Ga phosphate glasses studied (experimental points: dots; model function calculated according to the first-neighbor peaks: solid lines).

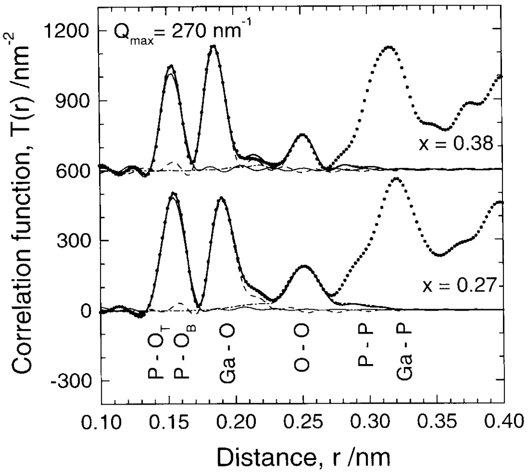


Fig. 2. Real-space correlation function $T(r)$ of the Ga phosphate glasses studied (experimental data: dotted lines; model function obtained by Gaussian fitting: heavy solid lines). The partial contributions are given with P-O: thin solid lines; Ga-O: dashed lines; O-O: dash-dotted lines.

3. Results

Weighted interference functions of the two samples are shown in Figure 1. Due to the use of high-energy photons (120 keV) of an intense source data are available up to more than 300 nm^{-1}, but the structure factors, $S(Q)$, showed reasonable behavior only up to $\sim$270 nm^{-1}. Data of higher Q are very noisy.

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

$$T(r) = 4\pi r\rho_0 + \frac{2}{\pi}\int_0^{Q_{\max}} Q[S(Q)-1]\sin(Qr)\,\mathrm{d}Q, \quad (1)$$

where ρ_0 is the number density of atoms. The values of ρ_0 are estimated when performing the FT procedures. The r-range of the $T(r)$ function in front of the first distance peak must oscillate about the zero line. Densities of 70 and 80 nm^{-3} were found to comply with this requirement for the glasses with $x = 0.38$ and 0.27, respectively. Note that the corresponding number densities of the related crystals GaPO_4 [2] and $\text{Ga(PO}_3)_3$ [7] are 72.0 nm^{-3} and 85.2 nm^{-3}, respectively. The final $T(r)$ functions are shown in Fig. 2 where the $Q_{\max}$ used in FT is 270 nm^{-1}.

Parameters of the first-neighbor distance peaks are determined by Gaussian fitting. The effects of the upper integration limit at $Q_{\max}$ in the FT are taken into account [23]. Here, in case of the X-ray data the weighting factors depend on Q. For fitting the $T(r)$ data, the Marquardt algorithm [24] was applied. Coordination numbers N_{ij}, mean distances r_{ij}, and full widths at half maximum (fwhm) Δr_{ij}, 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). Split P-O peaks were found for all phosphate glasses which have been studied by neutron diffraction experiments of high resolving power ($Q_{\max} \cong$ 500 nm^{-1}) [25]. The numeral ratio of P-O bonds depends on the degree of network depolymerization. The ratio is calculated from the compositions and is fixed in the fits. A possible asymmetry of the Ga-O peak is approximated by use of two Gaussian functions where the resulting two r_{GaO} have no special meaning and cannot be related to definite coordination polyhedra of Ga atoms. The O-O peak at $\sim$0.25 nm appears well resolved and free of other correlations. However, satellite ripples of theP-P and Ga-P correlations at 0.30 and 0.32 nm might somewhat affect the $T(r)$ function in the r-range of the O-O peak. The resulting parameters of the first-neighbor model peaks are given in Table 1. Interference functions are calculated using these parameters and are compared with the experimental functions (cf. Fig. 1). A good agreement in the high-Q range, where only short-range order information is reflected, can be stated. In Fig. 2

Table 1. Parameters resulting from Gaussian fitting of the first-neighbor P-O, Ga-O and O-O peaks of the correlation function, $T(r)$, which is shown in Figure 2.

Atom pair	Coordination number	Distance (nm)	fwhm (nm)	Total coordination number	Mean distance (nm)
27 mole% Ga_2O_3 glass					
P-O	2.05*	0.1495(10)	0.012(2)	4.0*	0.1542(10)
	1.95*	0.1592(10)	0.012(2)		
Ga-O	4.05(10)	0.1890(10)	0.016(3)	6.0(2)	0.193(2)
	1.95(10)	0.2015(30)	0.022(4)		
O-O	5.2(3)	0.2520(20)	0.025(3)		
38 mole% Ga_2O_3 glass					
P-O	2.9*	0.1515(10)	0.010(2)	4.0*	0.1540(10)
	1.1*	0.1605(10)	0.012(2)		
Ga-O	4.15(10)	0.1853(10)	0.016(3)	4.6(2)	0.187(2)
	0.45(10)	0.2020(30)	0.020(4)		
O-O	3.5(2)	0.2508(20)	0.017(3)		

* The compositions were chosen to maintain a P-O coordination number of four.

the model $T(r)$ functions and also the partial $T_{ij}(r)$'s are compared with the experimental $T(r)$ data.

At first, glass compositions of x = 0.40 and 0.25 have been used [15] (Chapter 2.1). Peak fitting results in P-O coordination numbers of 4.2 and 3.9 and in Ga-O coordination numbers of 4.4 and 6.3, respectively. Since 4.2 is outside the typical uncertainty of N_{ij} of a first distance peak, when N_{PO} = 4.0 is expected we renormalized the glass compositions so that N_{PO} is four in both cases and started again with Gaussian fitting. The new compositions are x = 0.38 and 0.27, where final total Ga-O coordination numbers of 4.6 and 6.0 are obtained. All data given above are already calculated on the basis of these new compositions which includes the functions in Figs. 1, 2 and the parameters in Table 1.

4. Discussion

The quality of the diffraction results presented is excellent. This is possible due to ease of corrections and to data of high Q which are available at an intense beam of high-energy photons of a synchrotron source. Reliable information of the P-O, Ga-O and O-O first-neighbor peaks of Ga phosphate glasses is obtained without using additional constraints and assumptions. The peaks are well resolved. The differences of the P-O coordination numbers from four were attributed to uncertainties of the composition. Renormalization where N_{PO} = 4 is realized with improved compositions, makes no changes of distances and minor changes of other coordination numbers. So the decrease of N_{GaO} by more than unity when the Ga_2O_3 fraction is increased from 0.27 to 0.38 is beyond any doubt. The decrease of N_{GaO} is accompanied by an evident shortening of Ga-O distances (cf. Fig. 2). The glass with 0.27 mole% Ga_2O_3 reveals a mean r_{GaO} of 0.193 nm, while the glass with 0.38 mole% Ga_2O_3 has a mean r_{GaO} of 0.187 nm (cf. Table 1). The corresponding Ga-O distances of the $Ga(PO_3)_3$ [7] and $GaPO_4$ [2, 3] crystals with GaO_6 octahedra and GaO_4 tetrahedra are ∼0.195 nm and ∼0.180 nm, respectively. The distance r_{GaO} of the 27 mole% glass (N_{GaO} = 6.0) is close to that of GaO_6 octahedra [7], while r_{GaO} of the 38 mole% glass (N_{GaO} = 4.6) is close to the middle of Ga-O distances of the GaO_6 [7] and GaO_4 [2, 3] polyhedra.

Commonly, the O-O peak at ∼0.25 nm found for phosphate glasses is only due to edges of the PO_4 tetrahedra. Thus, the number N_{OO} depends on the glass composition. O_T and O_B sites have three and six nearest oxygen neighbors, respectively, and their ratio changes with modifier additions. N_{OO} is calculated with $24(1-x)/(5-2x)$ [25]. N_{OO} should be four at metaphosphate composition, and it decreases to ∼3.4 at pyrophosphate composition. For the two glasses studied, N_{OO} should be close to 3.93 and 3.51, while numbers of 5.2 and 3.5 are obtained (Table 1). A significant difference is found for the N_{OO} of the glass with 27 mole% Ga_2O_3. It remembers to the diffraction study of an $Al(PO_3)_3$ glass [26], where also a tail of the O-O peak was obtained. It was argued that the short edges of AlO_6 octahedra contribute to this peak. Edges of GaO_6 octahedra with Ga-O distances of 0.193 nm would cause a contribution to O-O correlations at ∼0.27 nm, while edges of GaO_4 tetrahedra with Ga-O distances of 0.180 nm have lengths of ∼0.29 nm. Only the shorter lengths of the octahedral edges can contribute to the right side of an O-O peak at ∼0.25 nm. The high fraction of GaO_6 octahedra in the glass with 27 mole% Ga_2O_3 causes the difference with the calculated N_{OO}, while for the glass with 38 mole% Ga_2O_3 a similar effect is not found.

Beyond the three first-neighbor peaks a next huge peak at ∼0.32 nm is evident in the $T(r)$ data shown in Figure 2. This peak originates from superposition of several partial correlations. A shoulder at ∼0.295 nm in the $T(r)$ data of the glass with 27 mole% Ga_2O_3 is attributed to P-P correlations. This feature nearly vanishes for the other glass, which is due to the disruption of infinitely long chains to short chains, whereby N_{PP} is reduced from two to unity. The decrease in the P-P coordination number, i. e. the change from long chains to short chain fragments, PO_4 dimers, and isolated groups, is verified by IR and Raman spectroscopy [15]. Studying a Ga phosphate glass close to the pyrophosphate composition a broad distribution of chain lengths with a maximum frequency for PO_4 dimers was found using high-performance liquid chromatography [26]. The main peak contribution at ∼0.320 nm comes from Ga-P correlations. Ga-Ga correlations can be neglected, which is discussed below. The calculation of the P-O-P bridging angle results in 136° when the lengths of P-O_B bonds together with r_{PP} of ∼0.295 nm are used. A same angle of 137° is obtained for P-O-Ga linkages when lengths of P-O_T and Ga-O bonds (r_{GaO} = 0.193 nm) together with r_{GaP} of ∼0.320 nm are used. In case of the glass of 38 mole% Ga_2O_3, the height of the peak at 0.320 nm is somewhat reduced. The peak broadens to its left flank, which even indicates a new contribution at ∼0.305 nm. This distance is explained with the increasing number of GaO_4 tetrahedra which are formed instead of GaO_6 octahedra. Since r_{GaO} is shorter in tetrahedra, also shorter Ga-P distances appear.

The strong change of the Ga-O coordination number in the range from metaphosphate to pyrophosphate compositions agrees with observations which were made for other phosphate glasses [10 - 14, 16]. The change was found to be an accompanying effect of the transition from a surfeit of terminal oxygen atoms with 'dangling' P-O_T bonds to a 'deficit', where Me's have to share the O_T's for their coordination [10 - 14]. Thus, the number M_{TO} of O_T's which is available for coordination of each Me is the critical number. For three-valent Me this ratio $M_{\mathrm{TO}} = n(\mathrm{O_T})/n(\mathrm{Me})$ is $(1 + 2x)/x$. In Fig. 3 this ratio M_{TO} is compared with the Ga-O coordination numbers observed. Additionally, the N_{MeO}'s of rare earth cations, RE^{3+}, [13, 14] and of Al^{3+} [16] are given. For the RE^{3+} the minimum coordination number is about six and, thus, for $x > 0.25$ the N_{REO} don't follow the M_{TO} line and REO_n polyhedra start to cluster. A different behavior appears for the smaller Me^{3+} such as Al or Ga, which are well accommodated in tetrahedral environments. The Me-O coordination number well follows the number M_{TO} in that range where glasses of these oxides are obtained.

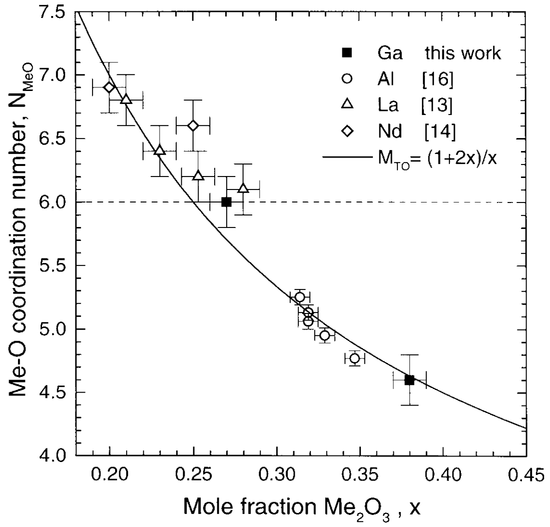
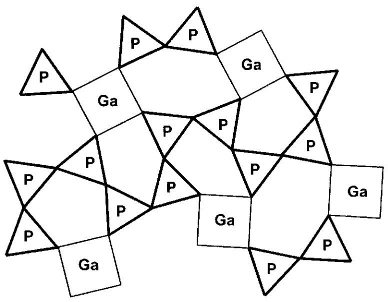


Fig. 3. Me-O coordination number vs. mole fraction of Me_2O_3 in glasses $(Me_2O_3)_x(P_2O_5)_{1-x}$ with Me = Ga [this work], La [13], Nd [14], Al [16]. The ratio $M_{\mathrm{TO}} = n(\mathrm{O_T})/n(\mathrm{Me})$ is given as heavy solid line. The dashed line at $N_{\mathrm{MeO}} = 6$ gives the lower limit of N_{LaO} and N_{NdO}, and the upper limit of N_{GaO} and N_{AlO} numbers.

The main structural features of the glasses studied where N_{GaO} is close to the M_{TO} line, i. e. close to $n(\mathrm{O_T})/n(\mathrm{Ga})$, are the massive formation of P-O_T-Ga bridges in addition to the P-O_B-P bridges, a lack of P-O_T bonds with O_T not having a second bond partner, a lack of O_T's which are shared between two GaO_n polyhedra, and also a lack of Ga-O-Ga bridges. $N_{\mathrm{GaO}} < M_{\mathrm{TO}}$ would result in P-O_T bonds with O_T not having a second bond partner while $N_{\mathrm{GaO}} > M_{\mathrm{TO}}$ would result in O_T's which are shared between GaO_n groups. Both features are unfavorable and are avoided when possible. A full transition from the above mentioned surfeit of O_T's to a clustering of MeO_n polyhedra due to shared O_T neighbors was found for earth-alkaline [10, 11] and RE phosphate glasses [12 - 14], but it is not detectable for Ga phosphate glasses due to the limited range of glass formation. P-O_T-Ga bridges as a main structural feature in Ga phosphate glasses have already been detected by Raman spectroscopy [15]. Also the appearance of high viscosities of the Ga phosphate melts was related [15] to the fact that oxygen atoms are mainly used in bridges, either in P-O-P or P-O-Ga links, thus all centers of structural PO_4 and GaO_n units are linked with bridges.

In order to visualize which features characterize the Ga phosphate networks the structures of the Ga meta-

25 mole% Ga_2O_3



40 mole% Ga_2O_3

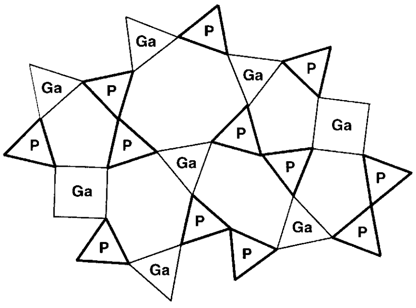


Fig. 4. Illustration of network changes from Ga meta- to pyrophosphate glasses. Triangles illustrate the tetrahedral units and squares stand for GaO_6 octahedra. All PO_4 tetrahedra link a further Ga site, all GaO_4 tetrahedra link a further P site and all GaO_6 octahedra link two further P sites vertical to the drawing plane.

and pyrophosphate glasses are illustrated in Figure 4. Due to problems in presenting three-dimensional networks in a plane, all tetrahedra are given as triangles and octahedra are given as squares. The incorporation of GaO_6 octahedra between highly meandering chains (25 mole% Ga_2O_3) results in dense arrangements of the polyhedral groups which is reflected by a high number density of atoms (80 nm^{-3}). At pyrophosphate composition (40 mole% Ga_2O_3), already 75% of the Ga atoms occupy tetrahedral sites and the network expands evidently, which is expressed in a smaller number density of atoms (70 nm^{-3}). Note, the number densities of atoms for networks formed of only tetrahedral groups whose four corners are linked with neighboring groups via bridges are even smaller. Values of $\sim$66 nm^{-3} are known in case of vitreous silica or of $\sim$63 nm^{-3} in case of vitreous germania.

The decrease of density with the change of N_{GaO} where P-O_T-Ga bridges are maintained demonstrates that the argument that the density increases when the phosphate network is disrupted from long to short chains, to PO_4 dimers and isolated groups is not appropriate. The compactation which is found for other polyphosphate glasses modified with, e. g., earth-alkaline and RE cations results from the ongoing process of sharing O_T's between two or three MeO_n polyhedra [10, 11, 13].

It is not possible to conclude the existence of GaO_5 polyhedra from diffraction data while the formation of AlO_5 units in Al polyphosphate glasses was shown by ^{27}Al NMR [16]. When GaO_5 units would exist, that would seriously interfere with any crystallization. A $Ga_4(P_2O_7)_3$ crystal, which so far is unknown, should contain 75% of Ga atoms in tetrahedra, the other part in octahedra, all that together with only PO_4 dimers. However, a mixture of different GaO_n units stabilizes the mixture of short chains, PO_4 dimers and isolated PO_4 groups which was found in the Ga pyrophosphate glasses [15, 26]. This behavior complicates the formation of a $Ga_4(P_2O_7)_3$ crystal and favours the separation of $GaPO_4$ phases.

5. Conclusions

Parameters of the P-O, Ga-O and O-O first-neighbor peaks of gallium phosphate glasses at meta- and pyrophosphate compositions are well determined using X-ray diffraction experiments of high resolving power. A strong decrease of Ga-O coordination numbers from 6.0±0.2 to 4.6±0.2 upon Ga_2O_3 additions is detected, which is accompanied by clear shortening of Ga-O separations. Only GaO_6 octahedra exist at metaphosphate composition. Close to the pyrophosphate composition, already a majority of Ga atoms (75%) is found in tetrahedral sites. The Ga-O coordination number behaves equivalently with the ratio $M_{\mathrm{TO}} = n(O_T)/n(\mathrm{Ga})$, thus, with the number of terminal oxygen atoms (O_T) in P-O_T bonds which are available for coordination of each Ga atom. This relation leads to conlcude that P-O_T-Ga bridges are formed for all O_T atoms. The shorter the formed phosphate chains, the more the network expands. This strange behavior is due to the change from GaO_6 octahedra to GaO_4 tetrahedra as the bridging units. The GaO_n polyhedra neither share O_T atoms nor form Ga-O-Ga bridges.

Acknowledgements

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