

Me-O coordination numbers in Ga and Zn phosphate glasses from meta- to pyrophosphate compositions – a high-energy X-ray diffraction study

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In glassy silicate networks formed of corner-linked tetrahedral SiO₄ network units the valency of the Si atoms equals the Si-O coordination number. Other oxide glasses such as phosphate systems are found in different situation which leads to peculiar structural features and, thus, to ‘anomalous’ behavior of properties. The ratio of the coordination number, N_{MeO} , of the network-modifying cation Me^{v+} to the number, M_{TO} , of terminal oxygen atoms (O_T) available for coordination of each cation plays a critical role in phosphate glasses [1]. M_{TO} decreases with modifier additions. Minima packing densities are found for glass compositions with $N_{\text{MeO}} = M_{\text{TO}}$ [2,3]. For some of the modifier cations a decrease of N_{MeO} is detected in glasses just below these minimum compositions (Mg²⁺ [2], Zn²⁺ [3], Nd³⁺ [4], La³⁺ [5]) while N_{MeO} does not much change above these compositions (Mg²⁺ [6]) where packing densities strongly increase.

By help of diffraction experiments performed on BW5 we tried to extend the knowledge of the behavior of N_{MeO} 's to confirm our concept of structural changes in phosphate glasses [1,3]. The twofold corner-linked PO₄ tetrahedra of metaphosphate glasses form chains and/or rings while singly corner-linked PO₄ units dominate at pyrophosphate composition and form P₂O₇ groups. With possible N_{GaO} 's from four to six a decrease of N_{GaO} from six to five is expected according to $M_{\text{TO}} = N_{\text{GaO}}$ in the change from meta- to pyrophosphate composition. On the other hand, for Zn phosphate glasses of the same compositional range no essential changes of N_{ZnO} should occur because the composition with $M_{\text{TO}} (N_{\text{ZnO}}) = 4$, the minimum possible coordination number, is already passed. The high-energy photons of BW5 allow a sufficient measuring range (Q -range) up to 250 nm⁻¹ (figs. 1a and 2a). After Fourier transformation of the scattering intensities that yields well resolved Ga-O and Zn-O distance peaks (figs. 1b and 2b) which are sufficient for accurate determinations of the N_{MeO} 's. With further increase of measuring time a Q_{max} of more than 300 nm⁻¹ could be achieved, however, then we would have to reduce the number of samples studied.

The P-O coordination number is four in case of all samples. The obvious changes of the heights of P-O peaks are due to changes of the P₂O₅ fraction. Thus, the increase of the heights of the Me-O peaks might also be due to the increase of Me fractions. This is clarified by modelling the peaks in the $T(r)$ functions. All Zn-O and Ga-O peaks except of those of the Zn phosphate glasses of $x = 0.50$ and 0.55 require approximation with two Gaussian functions in order to simulate their asymmetry.

The obvious decrease of the mean Ga-O distance (fig. 1b) with increasing x is a clear indication for the decrease of N_{GaO} . Actually, N_{GaO} decreases from 6.1±0.3 to 5.0±0.3 which is accompanied with a decrease of distance r_{GaO} from 0.191 to 0.186 nm. The error bars include already the uncertainty of the Ga₂O₃ fraction which is about ±2 mole%. An N_{GaO} of six stands for octahedral Ga environments while for N_{GaO} of five mixtures of GaO₄, GaO₅ and GaO₆ units are assumed.

The N_{ZnO} and r_{ZnO} possess a little increase from 3.9±0.2 and 0.194±0.001 nm to 4.2±0.2 and 0.200±0.002 nm, respectively, when the ZnO fraction is increased. The increase of r_{ZnO} is mainly due to the asymmetry of the Zn-O peak occurring for the glasses with ZnO fractions of 0.64 and 0.70. We would attribute this asymmetry to the change of the character of the O_T sites which are in P-O_T-Zn bridging positions for metaphosphate glasses but an increasing number of these O_T sites must accept two Zn neighbors with further ZnO additions.

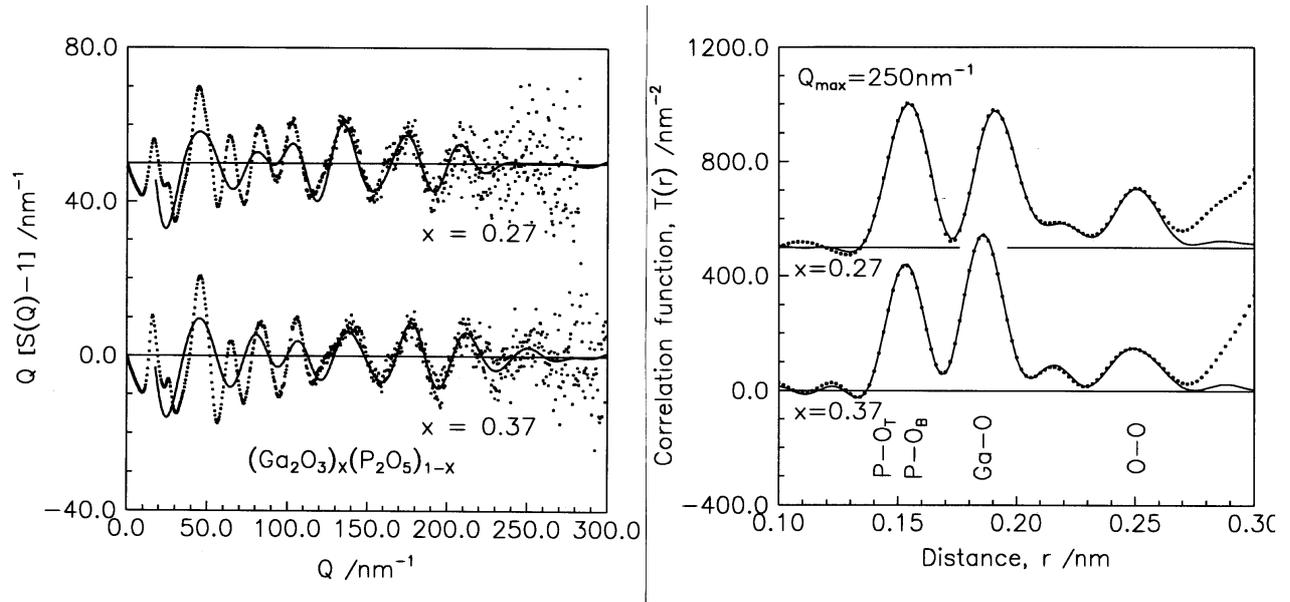


Figure 1: Weighted interference functions (a, left) and correlation functions (b, right) of Ga phosphate glasses of compositions close to the meta- and the pyrophosphate ones ($x = 0.25$ and 0.40). Dots represent the experimental data while solid-lined functions are due to fits of the P-O, Me-O and O-O first-neighbor peaks. The glass compositions are indicated in the plots.

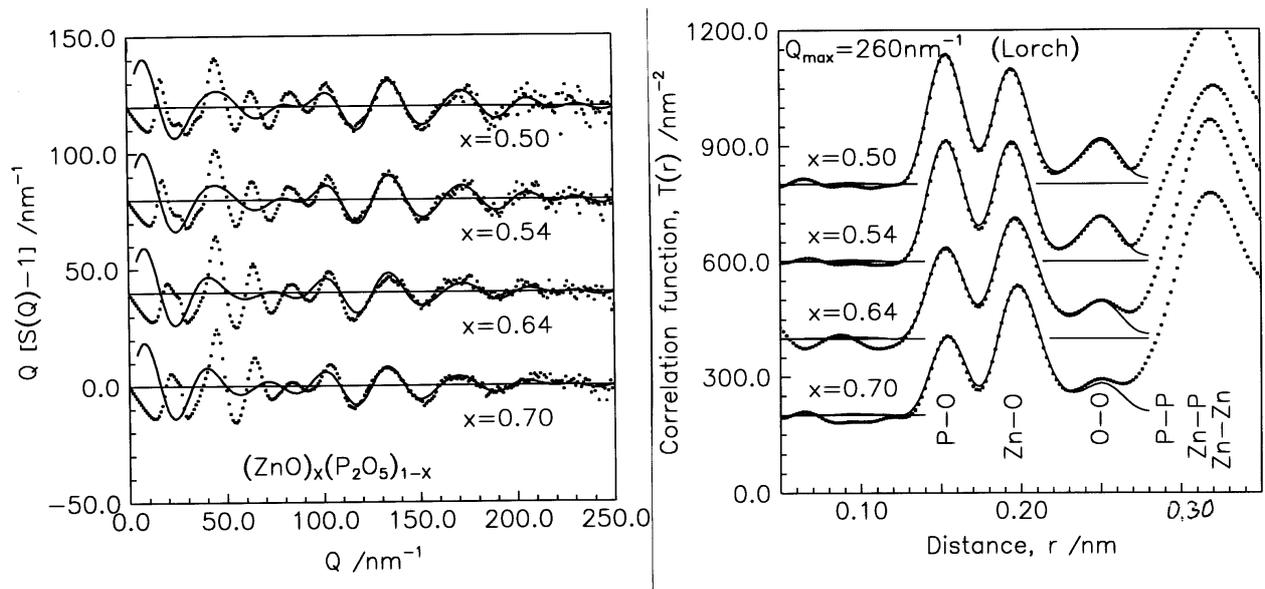


Figure 2: Weighted interference functions (a, left) and correlation functions (b, right) of Zn phosphate glasses of four compositions from meta- ($x = 0.5$) to beyond the pyrophosphate ones ($x = 0.66$).

References

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