

Effect of composition changes on the structure and properties of phosphate glasses in the pyrophosphate region

Jürgen Vogel and Peter Wange

Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität, Jena (Germany)

Peter Hartmann

Institut für Optik und Quantenelektronik, Friedrich-Schiller-Universität, Jena (Germany)

The structures of phosphate glasses in the ultra- and polyphosphate region are well-investigated. Discontinuous changes of the properties in the composition range around 50 mol% P_2O_5 (transition from network to chain-like structures) are known. The present work is concerned with the structural transition of chain-like phosphate glasses to pyrophosphate glasses. ^{31}P MAS NMR investigations were used for the quantitative structural analyses of pyrophosphate and mixed pyrophosphate/orthophosphate glasses. Several chemical and physical properties of these glasses were determined in dependence on composition and structure. The investigated phosphate invert glasses are very sensitive to additives. Therefore, some important properties of phosphate invert glasses and glass-ceramics can be controlled by addition of relatively small and highly charged cations.

Einfluß von Zusammensetzungsänderungen auf die Struktur und die Eigenschaften von Phosphatgläsern des Pyrophosphatbereiches

Die Strukturen von Phosphatgläsern im Ultra- und Polyphosphatbereich sind gut untersucht. Diskontinuierliche Eigenschaftsänderungen bei Gläsern mit P_2O_5 -Stoffmengengehalten um 50% (Übergang von Netzwerk- zu kettenähnlichen Strukturen) sind ebenfalls bekannt. Die vorliegende Arbeit beschäftigt sich mit dem strukturellen Übergang von kettenähnlichen Phosphatgläsern zu Pyrophosphatgläsern. ^{31}P -MAS-NMR-Untersuchungen wurden durchgeführt, um die Struktur sowohl von Pyrophosphat- als auch von gemischten Pyrophosphat/Orthophosphatgläsern quantitativ aufzuklären. Verschiedene chemische und physikalische Eigenschaften dieser Gläser wurden in Abhängigkeit von Zusammensetzung und Struktur bestimmt. Sie sind durch Zusätze vorzugsweise kleiner, hochgeladener Kationen gut steuerbar.

1. Introduction

Though the technical importance of pure phosphate glasses was small in the past, their structures were investigated intensively [1 to 3]. The poor chemical stability of numerous phosphate glasses makes structural analyses easy to carry out and permits e.g. the use of paper chromatography [4 to 6]. Because of some special optical and biological properties, phosphate glasses and glass-ceramics have recently gained importance in laser technique, several optical systems and in medicine. In the last years, these applications have resulted in numerous investigations of phosphate glass structures and properties using various methods of measurement [7 to 13].

Corresponding to their structures phosphate glasses can be divided into three groups: acidic phosphate glasses (ultraphosphate glasses) consist of three-dimensional networks of PO_4 tetrahedra. However, at most three corners of each tetrahedron are connected via bridging oxygen, otherwise the structure is analogous to SiO_2 glass. Therefore, merely glasses with more than 50 mol% P_2O_5 form phosphate networks. Polyphosphate

glasses containing 50 mol% P_2O_5 or less are formed by PO_4 tetrahedra chains (rings) possessing different chain lengths. Their structures are similar to those of organic polymers. By contrast, phosphate invert glasses are formed by ortho- and pyrophosphate structural groups exclusively [11, 14 and 15]. In these cases the glassy state is neither caused by a relatively stiff network structure nor by entangled chains, but by the interaction of differently charged cations.

Within these structural groups most of the properties of glasses change continuously. However, in the composition range around 50 mol% P_2O_5 , investigations of binary alkaline earth phosphate glasses by Kordes et al. [16] showed discontinuous changes of the properties.

The present investigation is concerned with the structural transition of chain-like phosphate glasses to pyrophosphate glasses and its effect on some of the physical and chemical properties. The selected glasses are base glasses for the development of resorbable phosphate invert glasses (system $P_2O_5-CaO-Na_2O-MgO$), and of bioactive long-term stable phosphate glass-ceramics (system $P_2O_5-CaO-Na_2O-Al_2O_3-(FeO/Fe_2O_3)$), respectively.

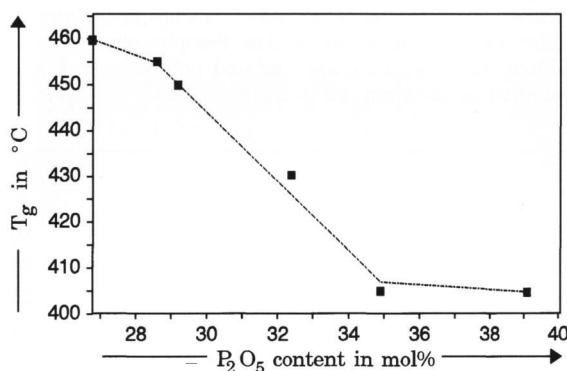
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Table 1. Compositions (in mol%) of glasses in the system $P_2O_5-CaO-Na_2O-MgO(-Al_2O_3)$

| glass designation | P_2O_5 | CaO | Na_2O | MgO | Al_2O_3 |
|-------------------|----------|------|---------|------|-----------|
| G 0 | 39.1 | 29.8 | 28.8 | — | 2.3 |
| G 2.5 | 34.9 | 27.4 | 29.0 | 6.5 | 2.3 |
| G 5 | 32.4 | 27.3 | 27.3 | 12.1 | 1.0 |
| G 7.5 | 29.2 | 26.3 | 25.2 | 16.8 | 2.5 |
| G 10 | 28.6 | 26.1 | 24.7 | 18.7 | 1.9 |
| G 12 | 26.8 | 24.0 | 22.7 | 24.9 | 1.7 |

Table 2. Compositions (in mol%) of glasses in the system $P_2O_5-CaO-Na_2O-Al_2O_3(-FeO/Fe_2O_3)$. The total content of iron was converted into mol% FeO

| glass designation | P_2O_5 | CaO | Na_2O | Al_2O_3 | FeO |
|-------------------|----------|------|---------|-----------|-----|
| GW 1 | 40.0 | 25.7 | 21.4 | 8.0 | 4.9 |
| GW 2 | 38.5 | 26.4 | 21.9 | 8.2 | 5.0 |
| GW 3 | 36.9 | 27.0 | 22.5 | 8.4 | 5.1 |
| GW 4 | 35.2 | 27.8 | 23.1 | 8.7 | 5.3 |
| GW 5 | 34.8 | 28.0 | 23.2 | 8.7 | 5.3 |
| GW 6 | 34.4 | 28.1 | 23.4 | 8.8 | 5.3 |
| GW 7 | 33.9 | 28.3 | 23.6 | 8.8 | 5.4 |
| GW 8 | 33.5 | 28.5 | 23.7 | 8.9 | 5.4 |

Figure 1. Transformation temperature of glasses in the system $P_2O_5-CaO-Na_2O-MgO(-Al_2O_3)$ as a function of the P_2O_5 content. The difference between the glasses G 2.5 (34.9 mol% P_2O_5) and G 7.5 (29.2 mol% P_2O_5) amounts to 45 K.

2. Experimental

2.1 Glass preparation

The investigated glasses were prepared by melting mixtures of carbonates and metaphosphates of calcium, sodium and magnesium, iron oxalate and $Al(OH)_3$ in Al_2O_3 crucibles using an electrically heated furnace. The melts were poured into water and remelted in platinum crucibles at 1300°C for 1 h. After casting, the surfaces of the glasses were quenched to prevent surface crystallization. The compositions are given in tables 1 and 2. Glasses of the system $P_2O_5-CaO-Na_2O-MgO$ possess up to 3 wt% Al_2O_3 due to corrosion of the crucibles.

2.2 Structure analyses by ^{31}P NMR

Structures of phosphate glasses can be described by connected Q^n groups (PO_4 tetrahedra). n gives the number of bridging oxygen atoms in the PO_4 tetrahedra and is determined by the degree of condensation. Different degrees of condensation result in different shielding of the phosphorus nuclei and, thus, in different values of the ^{31}P chemical shift anisotropy ($\Delta\delta$). Additionally, a correlation between the isotropic chemical shift (δ_{iso}) and the electric field strength of the cations surrounding the phosphate anions exists [17 and 18]. Thus, the ^{31}P NMR (Nuclear Magnetic Resonance) parameters are well-suited to identify both the different phosphate units and the cation influence on these structural groups. Information about the ordering state of the investigated materials can be obtained by analyzing the MAS (Magic Angle Spinning) line width.

The ^{31}P NMR spectra were acquired on the NMR spectrometer AMX 400 (Bruker GmbH, Rheinstetten (Germany)) (MAS rotation rates up to 15 kHz). A single-pulse sequence ($\pi/2$ pulse lengths of $t_w = 1.5 \mu s$, delay times $t_{de} = 10 \mu s$ and recycle times $t_{re} = 200 s$) was used. The ^{31}P chemical shift tensor parameters were obtained from slow-spinning MAS spectra (rotational frequency $\nu_r = 4$ to 5 kHz) [19]. The chemical shifts refer to a solution of phosphoric acid (85%). Because of the well-known effect of nuclear spin/electron spin interactions in iron-containing glasses, the informative value of NMR investigations on iron-containing glasses is low. Therefore, the authors resigned NMR measurements in the case of iron-doped glasses.

2.3 Determination of physical and chemical properties

Densities were determined on solid samples of a few grams using the Archimedes' method. The immersion fluid was benzene. Thermal expansion measurements were made at a heating rate of 10 K/min using a dilatometer 402 ES (Netzsch GmbH, Selb (Germany)). The transformation temperature of the glasses was determined by a differential thermal analyzer DTA 50 (Shimadzu, Kyoto (Japan)) with a heating rate of 10 K/min. Information about the chemical stability of the glasses was obtained by a thermal treatment of glass powders in 50 ml boiling distilled water (1 h). The powders possess a grain size of 0.50 to 0.315 mm. The powder was filtered and the dissolved ions in the residual solution were titrated with [$c(HCl) = 0.01 \text{ mol/l}$] [20].

3. Results and discussion

3.1 Phosphate glasses of the system

$P_2O_5-CaO-Na_2O-MgO(-Al_2O_3)$

Figure 1 gives the transformation points (T_g) of the glasses in dependence on their P_2O_5 content. In the range below 35 mol% P_2O_5 a discontinuous change of

T_g can be observed. Whereas the transformation points of the glasses G 0 and G 2.5 are nearly constant, a strong ascent in T_g between the glasses G 2.5 and G 7.5 is observable. The difference amounts to 45 K. Further decrease of the P_2O_5 content results only in a slightly increase of T_g .

Discontinuous changes of the thermal expansion and the chemical stability as a function of the P_2O_5 content of glasses can also be noticed (figures 2 and 3). In all the cases the graphs show a break in the range below 35 mol% P_2O_5 . This points to significant structural changes of the phosphate glasses. Therefore, ^{31}P MAS NMR investigations were used to obtain information about the real structure of the glasses. The ^{31}P MAS NMR spectra of some selected glasses possessing different P_2O_5 contents are presented in figure 4. All spectra show an intensive line at the position $\delta_{iso} = (-6.6 \pm 0.6)$ ppm. In consideration of the corresponding value of the ^{31}P chemical shift anisotropy $\Delta\delta = (137 \pm 6)$ ppm this signal can be attributed to Q^1 groups, influenced by calcium and sodium ions. The line at (-20.4 ± 0.6) ppm, observable in the spectra of the glasses G 0 (no. 1) and G 5 (no. 2), can be attributed to Q^2 groups due to their chemical shift anisotropy $\Delta\delta = (-176 \pm 6)$ ppm. However, the share of the Q^2 signal decreases proportional to the P_2O_5 content of the glasses and in the spectrum of glass G 12 (no. 3) Q^2 groups are not detectable. In this case a new line can be noticed, belonging to Q^0 groups with calcium and magnesium ions in their second coordination spheres ($\delta_{iso} = (1.4 \pm 1.2)$ ppm, $\Delta\delta = (35 \pm 10)$ ppm). In the spectrum this line forms a shoulder possessing a considerable intensity. The given shift tensor parameters were obtained by computer simulation of the spectra.

Table 3 gives the quantitative distribution of the different structural phosphate groups in the investigated glasses. The glasses G 0 and G 2.5 are formed by Q^2 and Q^1 groups. Q^2 groups, possessing two bridging oxygen atoms per PO_4 tetrahedron, are also called middle groups and form chains of PO_4 tetrahedra. Q^1 groups, possessing only one bridging oxygen atom, can be both end groups of the chains and PO_4 groups forming pyrophosphate groups. Although the share of Q^1 groups is significant higher compared with the Q^2 groups, the glasses G 0 and G 2.5 should be dominated by phosphate chain structures, because each phosphate chain requires two Q^1 groups. The share of "free" pyrophosphate groups should be low. By contrast, the glasses G 5 and G 7.5 predominantly consist of Q^1 groups forming pyrophosphate units. Only a few or no Q^2 groups are detectable.

This structural transition of chain-like phosphate glasses to pyrophosphate or mixed pyrophosphate-orthophosphate glasses (glass G 12) should increase the mobility of the ions strongly. However, the density, T_g and the chemical stability are increased and the thermal expansion is decreased in this range. Obviously, an ad-

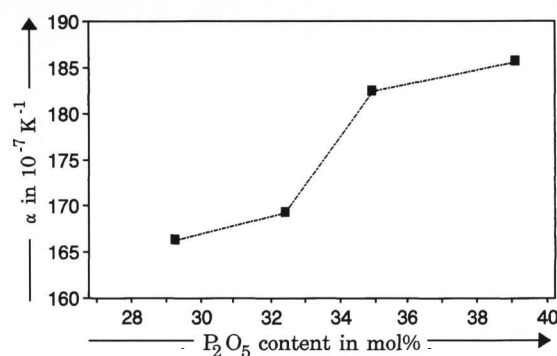


Figure 2. Thermal expansion of glasses in the system P_2O_5 -CaO-Na₂O-MgO(-Al₂O₃) as a function of the P_2O_5 content.

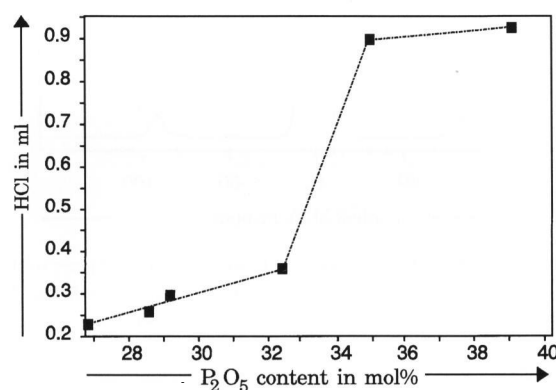


Figure 3. Chemical stability of glasses in the system P_2O_5 -CaO-Na₂O-MgO(-Al₂O₃) as a function of the P_2O_5 content. Glass powders (0.50 to 0.315 mm) were treated in 50 ml distilled water at 98 °C for 1 h. The dissolved ions in the filtered residual solution were titrated with $[c(HCl) = 0.01 \text{ mol/l}]$ [20].

ditional effect superimposes the changes of the phosphate structural elements.

The decrease of the P_2O_5 content in the system P_2O_5 -CaO-Na₂O-MgO(-Al₂O₃) was not achieved directly by reduction of P_2O_5 , but indirectly by increasing the MgO content. On the one hand, the resulting structural changes increase the mobility of the ions and the basicity of the phosphorus-bonded oxygens. On the other hand, in this way the tetrahedral coordination of magnesium is favoured compared with the octahedral one, resulting in a general stabilization of the glass structure. This explains the curves given in figures 1 to 3.

3.2 Phosphate glasses of the system P_2O_5 -CaO-Na₂O-Al₂O₃(-FeO/Fe₂O₃)

In this system the content of P_2O_5 was reduced directly. If the assumption mentioned in section 3.1 of the superimposed structural effects in the MgO-containing system is correct, a different correlation between properties and P_2O_5 content should be found in the new system. Figure 5 shows the transformation point T_g in dependence on

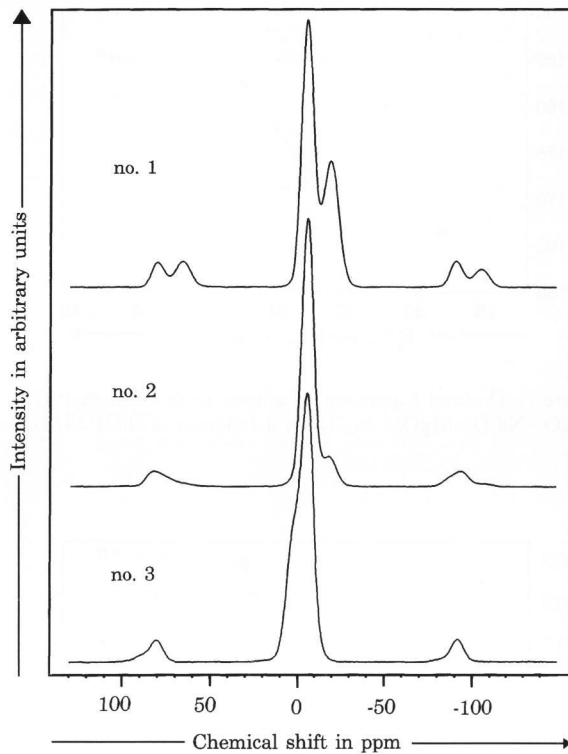


Figure 4. ^{31}P MAS NMR spectra of some selected glasses with different P_2O_5 contents; no. 1: spectrum of glass G 0, no. 2: spectrum of glass G 5, no. 3: spectrum of glass G 12.

Table 3. Distribution (in %) of Q^n structural groups in glasses of the system $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-MgO(-Al}_2\text{O}_3)$

| glass designation | Q^0 groups | Q^1 groups | Q^2 groups |
|-------------------|--------------|--------------|--------------|
| G 0 | = | 64 | 36 |
| G 2.5 | - | 79 | 21 |
| G 5 | ≈ 3 | 92 | ≈ 5 |
| G 7.5 | ≈ 7 | 93 | - |
| G 12 | 40 | 60 | - |

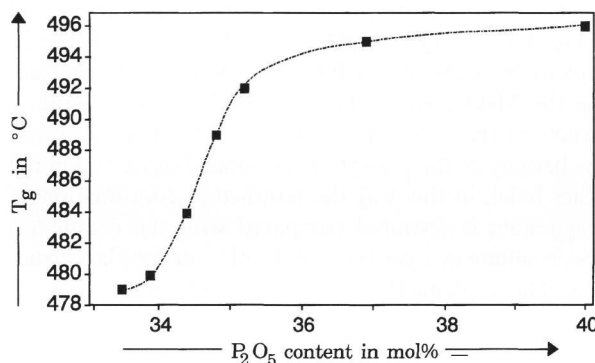


Figure 5. Transformation temperature of glasses in the system $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-Al}_2\text{O}_3\text{(-FeO/Fe}_2\text{O}_3)$ in dependence on the P_2O_5 content. The graph shows an increasing transformation temperature in the range of 34 to 37 mol% P_2O_5 with a discontinuity below 35 mol%.

the P_2O_5 content. The graph also shows a discontinuous course, however, in contrast to figure 1, T_g decreases

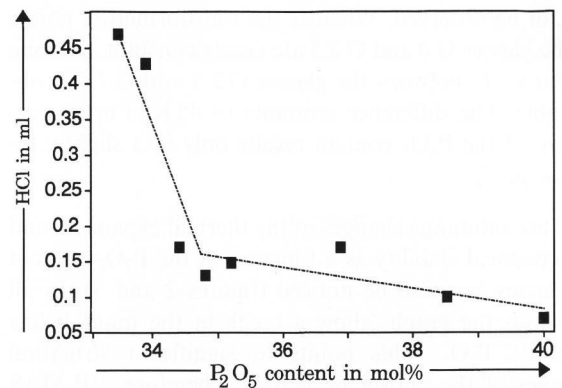


Figure 6. Chemical stability of glasses in the system $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-Al}_2\text{O}_3\text{(-FeO/Fe}_2\text{O}_3)$ as a function of the P_2O_5 content. The solubility in water increases discontinuously at P_2O_5 contents below 35 mol%.

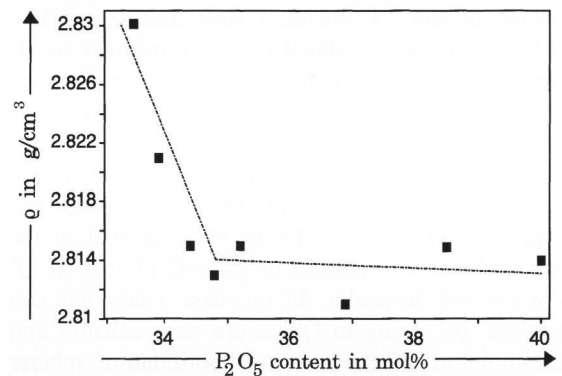


Figure 7. Density of glasses in the system $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-Al}_2\text{O}_3\text{(-FeO/Fe}_2\text{O}_3)$ as a function of the P_2O_5 content. The density increases discontinuously at P_2O_5 contents below 35 mol%.

with decreasing P_2O_5 content. Compared with the results given in figure 3, also a reversed dependence is observable in chemical stability (figure 6). These results meet the expectations and reflect the changes of the phosphate structures in the glasses. The smaller the degree of condensation, the higher is the mobility of the phosphate structural groups. This results in the observed increase of the solubility and decrease of the viscosity (expressed as T_g) in the transition range of chain-like phosphate glasses and pyrophosphate glasses. The increasing content of MgO in the glasses of the $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-MgO(-Al}_2\text{O}_3)$ system results in a stabilization of the glass structure superimposing the structural effects induced by decreasing P_2O_5 concentration. The glasses in the system $\text{P}_2\text{O}_5\text{-CaO-Na}_2\text{O-Al}_2\text{O}_3\text{(-FeO/Fe}_2\text{O}_3)$ possess a constant ratio of all network-modifying oxides, and the given curves (figures 5 and 6) reflect the pure influence of the changing structural phosphate units. The deviation in the course of the density graph (figure 7) does not contradict the other results. The increasing density in the range below 35 mol% P_2O_5 is explainable by the forming of small

structural phosphate units. In this way a more compact arrangement of the structural groups is sterically feasible.

4. Conclusions

The reduction of the P_2O_5 content in pure, silicon-free phosphate glasses results in a significant decomposition of the chain-like structure. Below 35 mol% P_2O_5 this structure is transformed to a phosphate invert glass structure, determined by ortho- and pyrophosphate groups exclusively. These structural changes effect discontinuities of several physical and chemical properties. Their appearance depends on the P_2O_5 content, but it is largely independent of the other ions in the glasses. However, the absolute values of the properties can be varied over a wide range by addition of relatively small and highly charged ions like Mg^{2+} , Al^{3+} or Ti^{4+} . These effects were utilized for the development of both bioactive and resorbable phosphate invert glasses and glass-ceramics.

5. References

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Adresses of the authors:

J. Vogel, P. Wange
Friedrich-Schiller-Universität
Otto-Schott-Institut für Glaschemie
Fraunhoferstraße 6, D-07743 Jena

P. Hartmann
Friedrich-Schiller-Universität
Institut für Optik und Quantenelektronik
Max-Wien-Platz 1, D-07743 Jena