

Structural investigations of SiO₂-containing phosphate glasses¹⁾

Jürgen Vogel and Carsten Jana

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

Peter Hartmann

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

The incorporation of SiO₂ into phosphate glasses is interesting in view of the development of phosphatic biomaterials. The present investigation is concerned with the incorporation of SiO₂ into phosphate base glasses possessing different phosphate structures. Due to their structural characteristics, they can be classified into three groups: glasses with long phosphate chains or rings formed by Q² phosphate structural groups, glasses with shorter phosphate chains formed by Q² and Q¹ groups and glasses with phosphate invert glass structure, possessing ortho(Q⁰)- and pyrophosphate groups (two Q¹ groups) exclusively. The structures of these glasses in dependence on the incorporated silica were investigated by transmission electron microscopy and by ³¹P MAS NMR. The principles of incorporation are discussed.

Strukturuntersuchungen an SiO₂-haltigen Phosphatgläsern

Im Hinblick auf die Entwicklung phosphatischer Biomaterialien ist der Einbau von SiO₂ in Phosphatgläser mit unterschiedlichen Phosphatstrukturen besonders interessant. Entsprechend ihrem Aufbau können die Phosphatgläser in drei Gruppen eingeteilt werden: Gläser mit langen Phosphatketten (aufgebaut aus Q²-Gruppen), Gläser mit kürzeren Phosphatketten (Q¹- und Q²-Gruppen) und Gläser mit Phosphat-Invertglasstruktur (nur Ortho- und Diphosphatgruppen). Der SiO₂-Einbau in diese unterschiedlichen Phosphatstrukturen wurde mittels Transmissionselektronenmikroskopie und ³¹P-MAS-NMR untersucht. Die Einbauprinzipien von SiO₂ in Phosphatgläser werden diskutiert.

1. Introduction

In contrast to many silicate, borate or borosilicate glasses, the importance of phosphate glasses is relatively small. However, besides some silicophosphate glasses and glass-ceramics [1 to 3], they have gained importance in view of the development of implant materials. Today, the excellent biocompatible and bioactive properties of phosphatic implant materials are well known [4 to 6]. Kokubo [7], Anderson [8] and others have shown that the formation of a SiO₂ gel layer or of silanol groups on the surface of bioactive phosphosilicate glasses can promote the precipitation of apatite on the implant materials and thus, their bioactivity. Therefore, it is appropriate to investigate phosphate glasses doped with silicon oxide. The first step is to explore the principles of incorporating SiO₂.

Usually, in oxide glasses and crystalline compounds silicon is fourfold oxygen-coordinated. However, the presence of phosphorus can force the silicon to a higher coordination number. The sixfold oxygen coordination of silicon in crystalline silicon diphosphates has been for many years and the different polymorphs of Si₂P₂O₇ are

well investigated [9 and 10]. Sixfold-coordinated silicon in phosphate glasses was also detected [11]. Therefore, the incorporation of silicon into the phosphate glass structure can be described by two different models:

- incorporation of the silicon oxygen polyhedra into or between the [PO₄] tetrahedra chains,
- formation of separate structural elements containing [SiO₄] tetrahedra by phase separation.

Since the early sixties the incorporation of silicon into basic phosphate glasses has been investigated by paper chromatography. In model a), the dissolution of glasses in water results in a hydrolysis of the -P-O-Si- bonds and the shortened phosphate chains give different chromatograms. In contrast, the chromatograms of the phase-separated glasses analogous model b) should be similar to those of the corresponding SiO₂-free glasses, because the chain length of the phosphate structural groups are not influenced. Du Plessis [12] investigated the incorporation of silicon into calcium metaphosphate glasses. In dependence on an increasing SiO₂ content a decreasing average phosphate chain length was registered. Similar results were published by Ohashi et al. [13]. Their investigations of mixed sodium phosphate silicate glasses point to a substitution of [SiO₄] tetrahedra for [PO₄] tetrahedra in long phosphate chains. Finn et al. [14] found that the ratio Na₂O/SiO₂ influ-

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Table 1. Compositions (in mol%) of base glasses (analysis)

base glass	P ₂ O ₅	Al ₂ O ₃	CaO	MgO	Na ₂ O
no. 7	52.4	5.3	42.3	—	—
no. 4	40.5	—	30.8	—	28.7
no. 2	29.2	2.5	26.3	16.8	25.2

ences the average phosphate chain length in such glasses. After the hydrolysis the number of shorter chains is twice as high as the number of incorporated silicon atoms (at low silica contents). Therefore, the region around the middle of the phosphate chains seems to be the favored place for the phosphate-silicate substitution. In contrast, different investigations using Raman spectroscopy indicate phase separation as the favored principle of incorporation [15 and 16].

The present investigation is concerned with the incorporation of SiO₂ into phosphate base glasses classified into three groups: glasses with long phosphate chains formed by Q² phosphate structural groups (P₂O₅–CaO–Al₂O₃), glasses with shorter phosphate chains formed by Q² and Q¹ groups (P₂O₅–CaO–Na₂O) and glasses with phosphate invert glass structure, possessing ortho-(Q⁰) and pyrophosphate groups (two Q¹ groups) exclusively (P₂O₅–CaO–MgO–Na₂O–Al₂O₃).

2. Experimental

All glasses investigated were prepared by melting mixtures of carbonates and metaphosphates of calcium, sodium and magnesium, Al(OH)₃ and SiO₂ at 1350 to 1550 °C. To improve the homogeneity of the glasses, the melts were poured into cold water and remelted in platinum crucibles at the same temperature range as described above. After casting, the surfaces of the glasses were quenched to prevent surface crystallization. The compositions of the base glasses are given in table 1. Table 2 shows the nomenclature and the SiO₂ contents of the silica-doped base glasses.

The structures of these glasses were investigated by transmission electron microscopy (replica, TEM H8100, Hitachi Ltd., Tokyo (Japan)) and by ³¹P NMR. The ³¹P Magic Angle Spinning (MAS) spectra were acquired in a 9.3 T magnet (161.92 MHz resonance frequency), using a commercial AMX 400 NMR spectrometer

(Bruker). The ³¹P chemical shifts have been referred to 85% H₃PO₄. All ³¹P isotropic chemical shift parameters δ_{iso} and the relative line intensities were obtained from high-speed MAS spectra using spinning speeds of about 12 kHz. The anisotropy (Δδ) and asymmetry (η) parameters were obtained from low-spinning-speed (of about 2 kHz) MAS spectra using the method of Herzfeld and Berger [17]. For reference, all known silicon diphosphates and silicon orthophosphates were produced and characterized by X-ray diffraction, ³¹P MAS NMR and 2D Exchange NMR [10].

3. Results and discussion

The isotropic chemical shifts of the investigated crystalline silicon monophosphates and the silicon diphosphates are clearly outside the range typical of alkaline and alkaline earth phosphates. This implies the possibility of analyzing the incorporation of silicon into a phosphate structure by measuring the ³¹P chemical shift.

The investigation of base glass no. 7 by ³¹P MAS NMR has shown that this glass is formed by Q² groups exclusively [δ_{iso} = –30 ppm, Δδ = (–151 ± 16) ppm]. Corresponding to the content of 52.4 mol% P₂O₅ also small amounts of Q³ groups (branching points) should be detectable. However, branching points in phosphate glasses are relatively instable. Probably, they were changed to Q² groups by small amounts of water. The introduction of up to 30 mol% SiO₂ into this phosphate glass structure does not change the NMR spectra. The glasses 7/3 to 7/30 (see table 2) show isotropic chemical shifts of around –30 ppm and anisotropies of around –190 ppm, typical values for Q² groups influenced by calcium and aluminum. Figure 1 shows a replica electron micrograph of glass 7/20. Its structure is homogeneous and no phase separation is detectable. So it can be concluded that, at least up to 20 mol%, SiO₂ is integrated into the phosphate chains or rings as [SiO₄] tetrahedra forming Si–O–P bonds. However, it seems to be a contradiction that the expected influence of silicon on the ³¹P shift tensors could not be observed. Even for silicon contents of 20 mol% the isotropic shifts of the Q² groups are nearly unchanged. Obviously, the incorporation of silicon into the phosphate short-range structure is different compared with crystalline silicon diphosphates. In general, there are two different possibilities for the incorporation of silicon into the phosphate chain or ring structures. The silica added could form Si–O–P

Table 2. Nomenclature and SiO₂ contents of the silica-doped base glasses

base glass	SiO ₂ content in mol%													
	0.5	1	1.5	2	3	4	4.5	5	6	9	12	15	20	30
no. 7	—	—	—	—	7/3	—	—	—	7/6	7/9	7/12	7/15	7/20	7/30
no. 4	—	—	—	—	4/3	4/4	4/4.5	4/5	—	—	—	—	—	—
no. 2	2/0.5	2/1	—	2/2	2/3	—	—	—	2/6	—	—	—	—	—

bonds between different phosphate chains (rings) or could substitute phosphorous positions (Q² groups) inside the phosphate chains. In the first case the short-range structure of the phosphorous positions in the chain (Q^{2+1Si} groups forming the Si–O–P bonds to another chain) is significantly changed. The electronic environments of these Q^{2+1Si} groups are similar to those of real Q³ groups. The isotropic shift should be changed significantly compared with Q² groups influenced by alkaline cations. Alternatively, SiO₂ could be incorporated by substituting phosphorus positions inside a given phosphate chain or ring. The Q² groups will then be transformed into Q^{1+1Si} (–P–O–P–O–Si–) or Q^{0+2Si} (–Si–O–P–O–Si–) groups. In fact, the electronic environments of the phosphorus atoms and therefore the isotropic chemical shifts are nearly unchanged. Respecting this, the almost unchanged ³¹P isotropic chemical shift parameters of the glasses 7/*X* (*X* = 3, 6, 9, 12, 15, 20) shows the direct incorporation of the silicon into the phosphate chains or rings.

IR investigations of the SiO₂-doped glasses (an additional band at 1100 cm⁻¹ is assigned to Si–O–P bonds [18]) and a strong increase of the solubility, caused by the relative low hydrolysis resistance of the Si–O–P bonds, support these results.

Figure 2 shows a replica electron micrograph of glass 7/30. In contrast to figure 1, a beginning faint phase separation can be observed. The glass 7/20 (composition in mol%: 44.3 P₂O₅, 20.0 SiO₂, 31.0 CaO, 4.7 Al₂O₃) possesses an atom ratio P/Si of 4.4 and chains or rings of [PO₄] tetrahedra can be built without any difficulties. The atom ratio of the glass 7/30 (composition (in mol%): 38.8 P₂O₅, 30.0 SiO₂, 27.1 CaO, 4.1 Al₂O₃) is only around 2.6. Obviously between the 20 and 30 mol% silica added there is a limit for the formation of phosphate silicate chain structures. Further increase of the SiO₂ content results not in a change of the phosphate structure, but in phase separation.

The P₂O₅ content of glass no. 4 is around 12 mol% lower compared with glass no. 7 and a considerable amount of sodium oxide was introduced. In the ³¹P MAS NMR spectrum of this glass two lines at $\delta_{\text{iso}} = (-20.4 \pm 0.6)$ ppm and $\delta_{\text{iso}} = (-6.6 \pm 0.6)$ ppm were observed. They are attributable to Q² and Q¹ phosphate structural elements, respectively, influenced by calcium and sodium ions. The quantitative ratio Q²/Q¹ is around 2, indicating shortened phosphate chains. Quantitative ³¹P MAS NMR investigations have shown that the Q²/Q¹ ratios of the glasses no. 4, 4/4 and 4/5 are identical within the error limits. Figure 3 shows a replica electron micrograph of glass 4/4. A pronounced phase separation is not observable, however, a base roughness of the glass structure has to be registered. The further increase of the SiO₂ content results in a marked phase separation (figure 4). Besides the phosphatic glass matrix a glassy drop-shaped phase enriched by silica can be observed. This result correlates with the investigations of the glasses possessing long chains. The mechanism of SiO₂

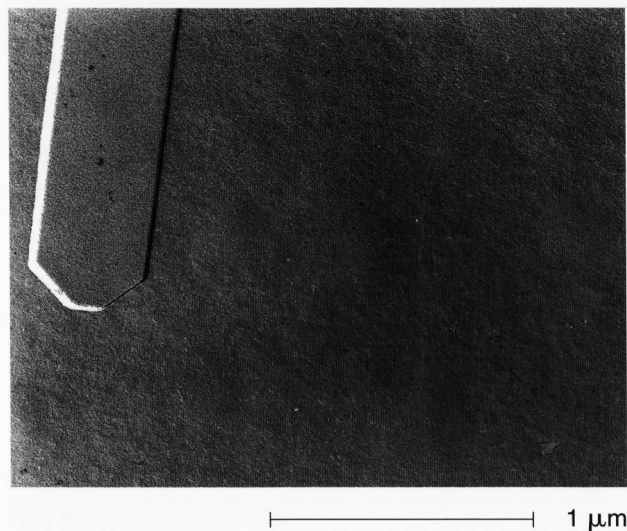


Figure 1. Replica electron micrograph of glass 7/20 (base glass no. 7 containing 20 mol% SiO₂). The comparison of the fractured surface with an MoO₃ crystal test plane demonstrates the homogeneous structure of the glass.

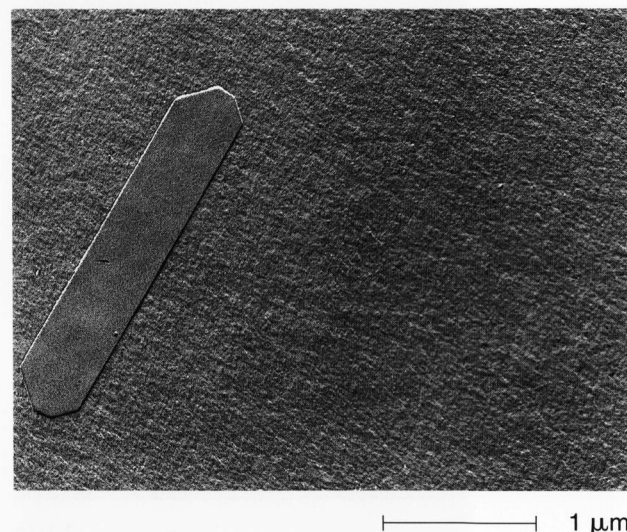
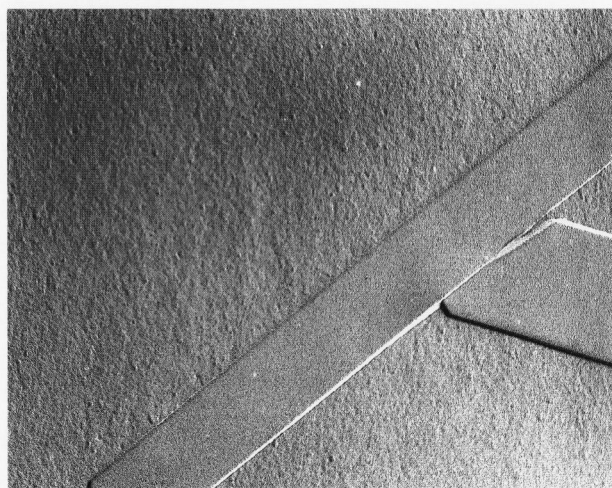


Figure 2. Replica electron micrograph of glass 7/30 (base glass no. 7 containing 30 mol% SiO₂). A base roughness of the glass structure indicates beginning phase separation.

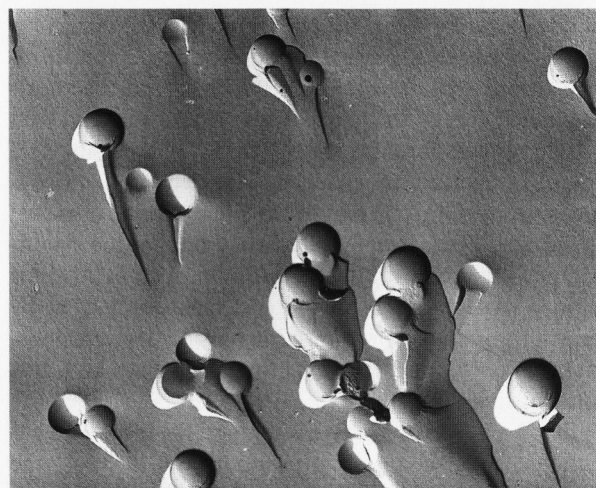
incorporation is the same as described above – the chain-like phosphate structure is retained. However, the phase separation takes place at lower SiO₂ contents, because the limit for the formation of chains is reached earlier in shorter phosphate chains.

To confirm these principles of incorporation, a phosphate invert glass was investigated. The integration of SiO₂ into such phosphate structures should be impossible. The ³¹P MAS NMR spectrum of glass no. 2 shows three lines at $\delta_{\text{iso}} = (-6.6 \pm 0.6)$ ppm, $\delta_{\text{iso}} = (0 \pm 0.6)$ ppm and $\delta_{\text{iso}} = (2.4 \pm 0.6)$ ppm. Because of the anisotropy $\Delta\delta = (137 \pm 6)$ ppm the line at -6.6 ppm can be attributed to Q¹ groups influenced by calcium and sodium. The



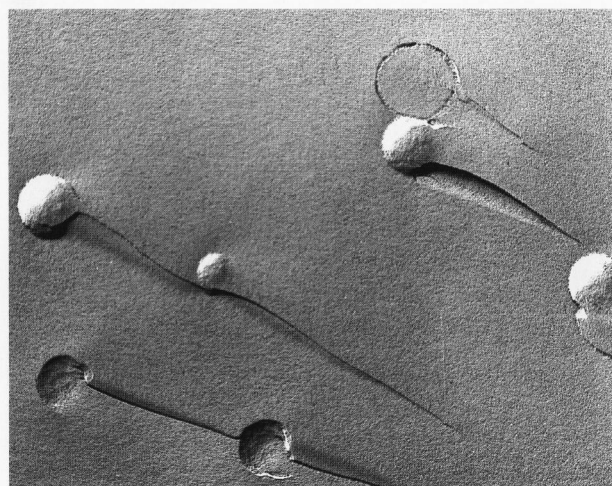
1 μm

Figure 3. Replica electron micrograph of glass 4/4 (base glass no. 4 containing 4 mol% SiO_2). A pronounced phase separation is not observable, however, a base roughness of the glass structure has to be registered.



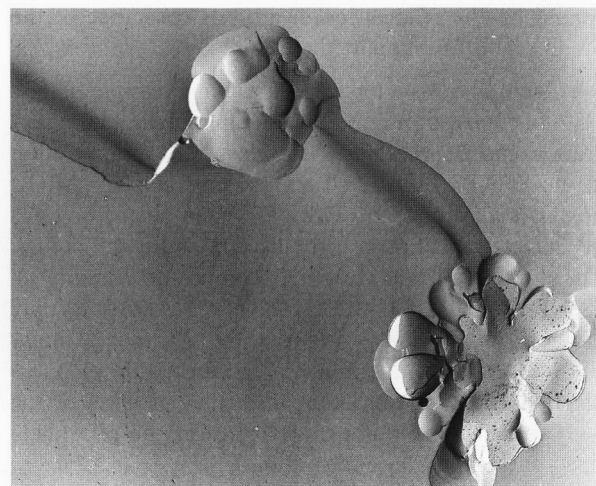
2 μm

Figure 5. Replica electron micrograph of glass 2/2 (base glass no. 2 containing 2 mol% SiO_2). Also small amounts of SiO_2 result in phase separation.



1 μm

Figure 4. Comparison of replica electron micrograph of glass 4/5 (base glass no. 4, containing 5 mol% SiO_2) with that of glass 4/4 (base glass no. 4 containing 4 mol% SiO_2) shows a marked phase separation.



5 μm

Figure 6. Replica electron micrograph of glass 2/2 (base glass no. 2 containing 2 mol% SiO_2). The droplet-shaped SiO_2 -enriched glassy microphase has the tendency to form blackberry-type aggregations.

other lines are caused by Q^0 groups influenced by magnesium (line at 0 ppm) and calcium ions (line at 2.4 ppm). This means the glass no. 2 contains ortho- and diphosphate groups exclusively possessing a ratio $Q^1/Q^0 = 93/7$.

The addition of 0.5 to 1 mol% SiO_2 to the base glass no. 2 results in the formation of visually clear glasses. However, TEM investigations have shown a pronounced roughness of the glass structure, indicating beginning phase separation. Figures 5 and 6 show replica electron micrographs of glass 2/2. Though the SiO_2 content is

low, an intensive phase separation can be observed. The droplet-shaped SiO_2 -enriched glassy microphase has the tendency to form blackberry-type aggregations, but the phase boundaries of the droplets are retained. The glassy matrix between these aggregations is homogeneous. Similar forms of phase separation were observed by Oliveira [19] and by Vogel [20] and a two-step phase separation process was discussed. But in the glasses investigated here not any indications of secondary phase separation could be found. Up to now, it has not been cleared unambiguously, why the droplets aggregate.

4. Conclusions

The manner of SiO₂ incorporation into phosphate glasses is mainly determined by the types of phosphate structural elements. The amount of Q² groups in the glasses controls the integration of the silicon oxygen polyhedra into the phosphate structural elements forming P–O–Si bonds. Glasses possessing long phosphate chains (or rings) integrate considerable amounts of SiO₂, but they retain the chain structure. The share of Q² groups (respectively Q^{1+1Si}) is constant within the error limits and it is independent of the SiO₂ amount added. In contrast, the investigated glasses possessing only a small share of (or no) Q² groups are not able to integrate SiO₂ and phase separation occurs. The presented results are in good agreement with those gained by paper chromatography.

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5. References

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■ 0498P003

Addresses of the authors:

J. Vogel, C. Jana
Friedrich-Schiller-Universität
Otto-Schott-Institut für Glaschemie
Fraunhoferstr. 6
D-07743 Jena

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