

Low- T_g phosphate glasses with improved water resistance for the coating of fluoride glass fibers¹⁾

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Starting from a multicomponent lead phosphate glass composition given in the literature, a glass was developed suitable for the protective overlaid of heavy-metal fluoride glass fibers. Besides a low glass transition temperature $< 270^\circ\text{C}$, a high thermal expansion coefficient $> 18 \cdot 10^{-6} \text{K}^{-1}$, the phosphate glass material developed had a water resistance at 60°C for 10 h comparable to that of commercial container glass. The final composition developed was (in mol%): 54.7 P_2O_5 , 19.8 PbO , 18.0 Na_2O , 1.2 MgO , 1.2 BaO , 1.2 CaO , 0.4 V_2O_5 , 1.5 Al_2O_3 , 2.0 Bi_2O_3 . Besides the influences of these different components the action of the melting conditions, especially melting temperature and trace SiO_2 content from the crucible material, have to be taken into account. Fiber drawing experiments including the in-situ application of the phosphate glass overlaid were successful.

Phosphatgläser mit niedriger Transformationstemperatur und verbesserter Wasserbeständigkeit für das Beschichten von Fluoridglasfasern

Ausgehend von einem Mehrkomponenten-Bleiphosphatglas erfolgte die Entwicklung einer geeigneten Beschichtung für Schwermetallfluoridgläser. Mit einem Glas der Zusammensetzung (Stoffmengenanteil in %): 54,7 P_2O_5 ; 19,8 PbO ; 18 Na_2O ; 1,2 MgO ; 1,2 BaO ; 1,2 CaO ; 0,4 V_2O_5 ; 1,5 Al_2O_3 ; 2 Bi_2O_3 konnten Wasserbeständigkeiten bei 60°C und 10 h Korrosionsdauer erreicht werden, die vergleichbar mit denen von Verpackungsgläsern sind. Die Transformationstemperatur dieses Glases liegt $< 270^\circ\text{C}$ und der Wärmeausdehnungskoeffizient $> 18 \cdot 10^{-6} \text{K}^{-1}$. Es wurden die Einflüsse der verschiedenen Komponenten und der Schmelzbedingungen untersucht. Von besonderem Interesse war der Einfluß der Schmelztemperatur und der SiO_2 -Gehalte im Glas, die durch Korrosion des Tiegelmaterials eingebracht wurden. Beschichtungsversuche nach dem Stabziehverfahren konnten erfolgreich durchgeführt werden.

1. Introduction

Low-water resistance is one of the main aspects limiting the commercial application of phosphate glasses. Few applications, such as solder glasses, glasses resistant against hydrofluoric acid, heat protection glasses or optical glasses for special applications, are known only. A great advantage of phosphate-based systems is the ability to vary the properties over a wide range. Thus, glass transition temperatures, T_g , vary from 130 to 600°C , as well as the thermal expansion coefficients, α_{20/T_g} , from 5 to $28 \cdot 10^{-6} \text{K}^{-1}$ [1 to 3].

A lot of efforts has been undertaken to overcome the poor chemical durability of phosphate glasses. Thus, Peng and Day [4 and 5] developed water-resistant glasses of the systems $\text{P}_2\text{O}_5\text{-M}_2\text{O}_3\text{-K}_2\text{O}$ (M = aluminum, gallium, indium, lanthanum, boron, iron, and bismuth) as sealing materials for high-expansion metals such as aluminum alloys and stainless steel. α values were $> 18 \cdot 10^{-6} \text{K}^{-1}$. Al_2O_3 , PbO , and Ag_2O additions led to a higher chemical durability, with the best results obtained with Al_2O_3 . CdO , ZnO , and V_2O_5 additions

increased the water resistance of lead phosphate glasses [6]. Similar durabilities were achieved with borophosphate glasses [1], while zinc phosphate glasses exhibited an even lower durability than lead phosphate glasses [7]. Another way to increase the water resistance is the nitridation of phosphate glasses [8]. Glass transition temperatures and microhardnesses increased, while the thermal expansion coefficients dropped. Sales and Boatner [9] developed lead-iron phosphate nuclear waste glasses with a hydrolytic resistance higher than that of borosilicate glasses. The influence of oxide additions to binary and multicomponent phosphate glasses has been investigated extensively and it could be demonstrated that α increases with increasing radius of the alkali and alkali earth ions [2, 9 and 10]. Al_2O_3 and B_2O_3 additions increase T_g and lower α , depending on the molar ratio of alkali earth oxide/ P_2O_5 [1 and 11]. Improved chemical durability could be measured also on WO_3 -containing glasses, whose additions exceed the effect of Al_2O_3 [2]. Indium and scandium oxide additions even effect a dramatic increase of the chemical durabilities in binary lead-indium and lead-scandium phosphate glasses, respectively [12]. A mixed alkali effect of these properties was observed on barium metaphosphate glasses [1 and 11]. Residual water from the melting process lowers T_g and increases the tendency to phase separation [13 and 14].

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The main emphasis of the present work was to develop stable and chemically resistant high-thermal expansion phosphate glasses as coating materials for heavy-metal fluoride glass fibers [15]. This family of glasses reached major interest because of their infrared attenuation losses, which were predicted to be about two orders of magnitude lower than those of commercial silica glass fibers [16]. Because of their extraordinary optical properties these fluoride glasses can possibly be candidates for long-distance telecommunication fibers. However, on the other hand, they are chemically and mechanically relatively unstable materials. Thus far, this problem could not be overcome by compositional variations of the fluoride systems. For this reason fluoride glass fibers must be coated for chemical and mechanical protection. In order to succeed with such a coating process, the properties of the two materials must be similar. If, as is the case here, a glass is used for coating, the α value of this glass has to be $> 18 \cdot 10^{-6} \text{ K}^{-1}$, the T_g value must lie $< 270^\circ\text{C}$, and a high chemical durability of the phosphate system used has to be guaranteed. Preferentially the water resistance at 60°C , L , has to be near $0.02 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$, a value comparable to that of commercial container glass.

2. Experimental

The phosphate glasses were prepared using di-ammonium-hydrogen-phosphate, Na_2CO_3 , K_2CO_3 , BaCO_3 , B_2O_3 (reagent grade; Merck, Darmstadt (Germany)), CaCO_3 , V_2O_5 (pure; Merck), PbO (99%; Riedel de Haen, Seelze-Hannover (Germany)), MgCO_3 (reagent grade; Riedel de Haen), Li_2CO_3 (Riedel de Haen), AlPO_4 (basic; Merck), Bi_2O_3 , and Nb_2O_5 (pure; Fluka AG, Neu-Ulm (Germany)). The glass batches were heat-treated and melted in 150 ml silica glass crucibles. To achieve moderate batch reactions the well-mixed batch for 50 g of glass was first heat-treated at 200, 300, and 400°C for 1 h each. Then the temperature was raised to 750°C and held for 1.5 h. The melt was poured then into preheated aluminum molds. T_g and α values were measured with a dilatometer (402 E; Netzsch, Selb (Germany)), with accuracies of $\pm 4 \text{ K}$ and $\pm 0.2 \cdot 10^{-6} \text{ K}^{-1}$, respectively. The water resistance, L , was determined using flat glass samples with surface areas between 4 and 8 cm^2 , which were immersed into 200 ml bi-distilled water at 60°C for different times up to 36 h. The samples were weighed before and after the corrosion experiment. The total weight loss was related to the sample surface and was evaluated in $\text{mg}/(\text{cm}^2 \cdot t_{\text{corrosion}})$, accuracy $\approx 15\%$. The remaining leach solutions were used to determine the heavy-metal release rates for lead, barium, cadmium, and vanadium by atomic absorption spectroscopy (PU 9200 and PU 9400, Philips, Kassel (Germany)), accuracies $\approx 4\%$. The conventional Knoop microhardness, $H_K 0.1/20$, was measured with a proof tester (HMV 2000, Shimadzu, Tokyo (Japan)), accuracy $\approx 3\%$. The refractive index, n_D , was obtained using a phase contrast microscope (Axioskop, Zeiss, Oberkochen

(Germany)), with an accuracy between $\pm 2 \cdot 10^{-4}$ and $5 \cdot 10^{-3}$. The density, ρ was measured pycnometrically, accuracy ± 0.01 to $0.04 \text{ g}/\text{cm}^3$. Samples with crystalline phases were checked by scanning electron microscopy (SEM), (JXA5, Jeol, Tokyo (Japan)) with EDX system (Ortec, München (Germany)). Crystalline phases were investigated by X-ray diffraction (XRD) (PW 1729; Philips, Kassel (Germany)), and the chemical analysis of the glasses was done by X-ray fluorescence (PW 1410; Philips) with an accuracy of ± 0.1 to $\pm 0.5\%$, depending on component.

3. Results

3.1. Preliminary experiments

After literature study three different glass systems seemed to be promising for further optimization (compositions in mol%):

- 61 P_2O_5 , 37 Na_2O , 2 Al_2O_3 [2]³⁾; $\alpha = 18.4 \cdot 10^{-6} \text{ K}^{-1}$, $T_g = 116^\circ\text{C}$;
- 70 P_2O_5 , 5 B_2O_3 , 5 Li_2O , 15 Na_2O , 5 MgO [1]; $\alpha = 15.4 \cdot 10^{-6} \text{ K}^{-1}$, $T_g = 127^\circ\text{C}$;
- 55.9 P_2O_5 , 20.6 PbO , 18.7 K_2O , 1.2 MgO , 1.2 BaO , 1.2 CdO , 1.2 V_2O_5 [6]; $\alpha = 20.5 \cdot 10^{-6} \text{ K}^{-1}$, $T_g = 211^\circ\text{C}$ (glass denoted PG I).

Although many efforts were undertaken to optimize the glasses of systems a) and b), e.g. stepwise replacement of P_2O_5 by Al_2O_3 and WO_3 , respectively, and the already mentioned substitution of Na_2O for K_2O , the final results obtained were not fully satisfactory, especially with respect to the chemical durability, for details see [17]. Therefore, the further work concentrated on the glass PG I. Since such a multicomponent glass does not allow global composition changes, the authors first tried to develop a maximum chemical durability, replaced the toxic component CdO , and reached then a final tuning of the properties.

3.2. Stepwise optimization

A simple method to improve glass properties may be seen in applying the mixed alkali effect, i.e. partially replacing one alkali oxide with another one. This was done in substituting Li_2O and Na_2O for K_2O of glass PG I successively. Figure 1 shows that the chemical durability of the new glass series is strongly enhanced, however, a special mixed alkali effect, which preferentially should show up as an extremum at a molar alkali oxide ratio of about 1:1, cannot be found. Similarly, a mixed alkali effect was not found either in the release rate of the heavy-metal compounds, see figure 2 for the case of the Li_2O -substituted glasses. The Na_2O -substituted glasses behaved nearly identically [17].

The next step was to prove whether the use of WO_3 in the glasses is more favorable than the use of V_2O_5 . For this the chemical durabilities of two glass series were

³⁾ The original glass system a) contains K_2O instead of Na_2O [2], which has been substituted here from the beginning in order to improve properties.

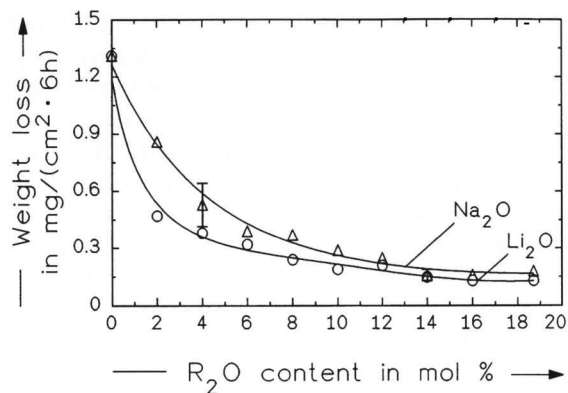


Figure 1. Water resistance of glasses at 60°C derived from glass PG I by substituting Li₂O and Na₂O for K₂O.

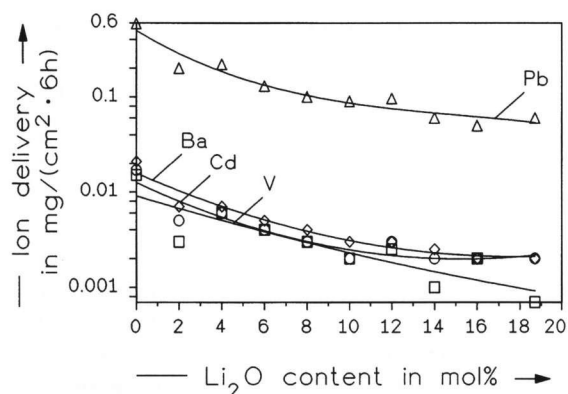


Figure 2. Heavy-metal release rate at 60°C from glasses derived from glass PG I by substituting Li₂O for K₂O.

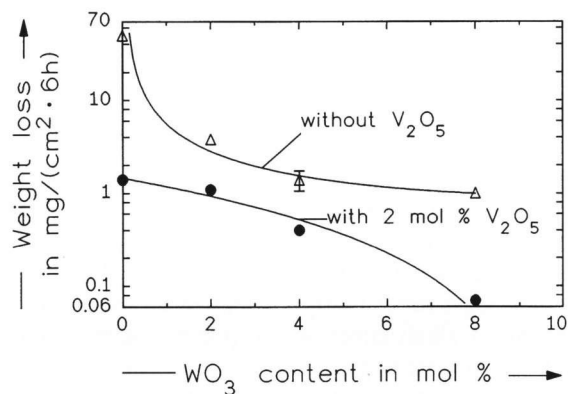


Figure 3. Water resistance of glasses at 60°C derived from glass PG I by substituting WO₃ for P₂O₅. Curve "without V₂O₅": The total V₂O₅ content was removed from the glasses; curve "with 2 mol% V₂O₅": The V₂O₅ content was set to this value.

tested (figure 3). In one case a V₂O₅-free glass was used, in the other case a glass containing 2% V₂O₅. The durabilities of both glass series increased with increasing WO₃ content, however, since both V₂O₅ and WO₃ may

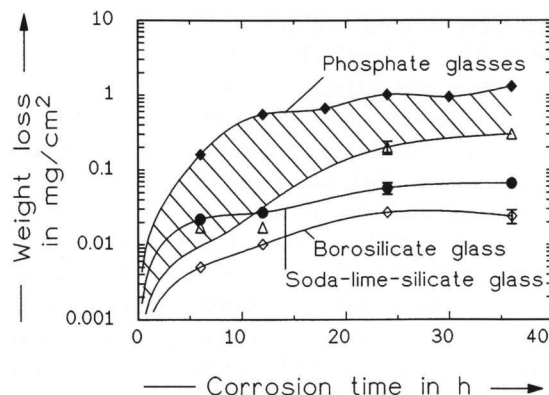


Figure 4. Water resistance of phosphate glasses at 60°C compared to that of commercial soda-lime-silica and borosilicate glasses. The hatched area represents the hydrolytic resistance being obtained during the different optimization experiments.

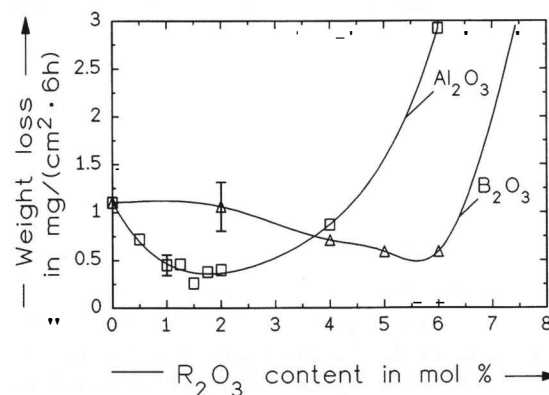


Figure 5. Water resistance of glasses at 60°C derived from glass PG II by substituting Al₂O₃ and B₂O₃ for P₂O₅.

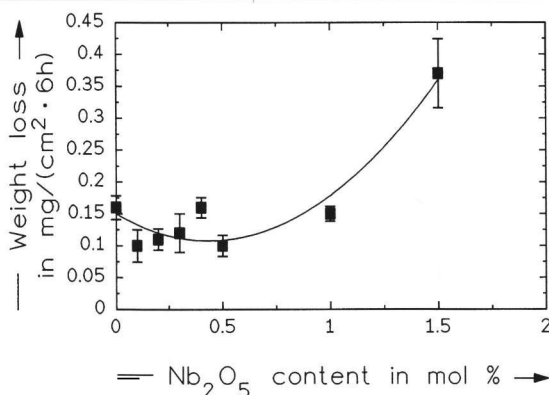
be regarded as network-forming oxides, both T_g and α increased too much, thus, these glasses may not be found suitable for the intended coating experiments.

The experiments described thus far showed that it should be possible to prepare a glass with an optimized chemical durability if in the glass PG I Na₂O is substituted for K₂O, and WO₃ is substituted for 8 mol% P₂O₅ (glass denoted PG Ia) (table 1). Figure 4 shows the water-leaching stability of this phosphate glass, compared to that of commercial container glass and borosilicate glass. As may be seen this phosphate glass developed has a stability comparable to that of container glass within a time period of about 12 h, and even commercial borosilicate glasses are not much better in this time span. However, the α value of glass PG Ia of $17.9 \cdot 10^{-6} \text{ K}^{-1}$ lies at the lower limit and the T_g value of 307°C is too high.

The toxic component CdO could be removed easily from the glasses by replacing it with an equimolar amount of CaO (glass denoted PG II). Measurable changes in L and α values did not occur, however, T_g was decreased to 199°C [17]. Further work concentrated therefore on the substitution of Al₂O₃ and B₂O₃ for

Table 1. Most important glass compositions developed, starting from glass PG I [6]. The table contains also some property data.

glass	glass composition (in mol%)												T_g in °C	α in 10^{-6} K^{-1}	L in $\text{mg}/(\text{cm}^2 \cdot 6 \text{ h})$
	P_2O_5	PbO	Na_2O	K_2O	MgO	BaO	CdO	CaO	V_2O_5	WO_3	Al_2O_3	Bi_2O_3			
PG I	55.9	20.6	=	18.7	1.2	1.2	1.2	=	1.2	=	=	=	211	20.5	1.20
PG Ia	47.9	20.6	18.7	—	1.2	1.2	1.2	—	1.2	8.0	—	—	307	17.9	0.02
PG II	56.0	20.5	—	18.7	1.2	1.2	—	1.2	1.2	—	—	—	199	20.5	1.10
PG III	54.5	20.5	18.7	—	1.2	1.2	—	1.2	1.2	—	1.5	—	233	19.8	0.16
PG IV	54.7	19.8	18.0	—	1.2	1.2	—	1.2	0.4	—	1.5	2.0	227	20.6	0.08

Figure 6. Water resistance of glasses at 60°C derived from glass PG III by substituting Nb_2O_5 for P_2O_5 .

P_2O_5 . It is known from silicate glasses that these components improve the chemical durabilities, and it has also been shown that binary alumophosphate and borophosphate glasses, as well as multicomponent borophosphate glasses are also influenced strongly [1]. Glass PG II (table 1) was taken as base for these experiments. Figure 5 shows the results. Both Al_2O_3 and B_2O_3 additions result in minima of the weight loss. Glasses beyond these minima displayed some crystalline inclusions. An SEM-EDX analysis showed a relative enrichment of phosphorus, lead, potassium, and vanadium in these crystals compared to the surrounding glass, but XRD was able to identify only the crystalline compound $\text{K}_3\text{P}_3\text{O}_9$ with certainty. When melting these glasses, increasing melt viscosities were observed. Table 2 shows that the physical properties of these modified glass compositions, especially T_g and α , are clearly matching the demanded limits.

The next step for an optimal glass development was done by replacing the total amount of K_2O of glass PG II with Na_2O and by substituting Al_2O_3 for 1.5% P_2O_5 (glass denoted PG III) (table 1). Al_2O_3 was used instead of B_2O_3 , since in that case a lower amount is necessary to increase the chemical stability (figure 5). The weight loss was $L = 0.16 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$, with $\alpha = 19.8 \cdot 10^{-6} \text{ K}^{-1}$ and $T_g = 233^\circ\text{C}$.

However, the value of the chemical stability obtained is still too high compared to the target value of $0.02 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$. Therefore, the further work was di-

rected to introduce components which strengthen the network to some extent. Candidates for this were WO_3 , Nb_2O_5 , and Bi_2O_3 , respectively. Figure 6 shows the durability results obtained when Nb_2O_5 is partially substituted for P_2O_5 in glass PG III (table 3). There is no clear effect on L up to about 1% addition; for Nb_2O_5 additions of more than 1%, the resistance becomes even less. Initial experiments with an equimolar exchange of Bi_2O_3 for PbO , which should enhance the cross-linking in the glass structure, did not succeed either. Up to 4% Bi_2O_3 the L values clustered near $0.14 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$. Therefore, a closer insight into the phosphate glass structure is necessary.

P_2O_5 , PbO , and Na_2O are the main components of the glasses discussed. Their network is formed by sodium-phosphate chains, mainly cross-linked by PbO . If the contents of P_2O_5 or PbO are changed, the whole structure is changed. Thus, the substitution has to be done in such a way that the molar ratios of the mentioned main glass components remain unchanged. This was done finally when Bi_2O_3 was introduced into the glasses in equimolar amounts for Na_2O , PbO , and P_2O_5 , respectively. The result is shown in figure 7. Chemical weight loss data of $\approx 0.05 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$ were obtained with Bi_2O_3 additions between 2 and 3%. T_g values of these glasses were 227°C and the α values increased from 19.5 (no Bi_2O_3) to $20.6 \cdot 10^{-6} \text{ K}^{-1}$ (3% Bi_2O_3). Higher Bi_2O_3 contents do not have further advantages, on the contrary, these glasses behave mechanically more brittle. In a final optimization step the V_2O_5 content could be reduced even to 0.4%. This action lowered the viscosity of this melt favorably, but the L , T_g , and α values of this glass (PG IV), which were $0.08 \text{ mg}/(\text{cm}^2 \cdot 6 \text{ h})$, 227°C , and $20.6 \cdot 10^{-6} \text{ K}^{-1}$, respectively, were fully satisfactory for the subsequent coating experiments. This optimized composition (in mol%) is given by 54.7 P_2O_5 , 19.8 PbO , 18 Na_2O , 1.2 MgO , 1.2 BaO , 1.2 CaO , 0.4 V_2O_5 , 1.5 Al_2O_3 , 2 Bi_2O_3 .

Table 1 summarizes compositions and properties of the glasses PG I to PG IV.

3.3. Influence of melting conditions

It is well-known that the properties of glasses depend to some extent on the conditions how the glasses were prepared. Water, for example, acts as a network modifier

Table 2. Glass compositions derived from glass PG II by substituting Al₂O₃ and B₂O₃ for P₂O₅. The table contains also some physical property data.

glass	glass composition (in mol%)									T_g in °C	α in 10^{-6} K^{-1}	$H_K 0.1/20$ in N/mm ²	n_D	ρ in g/cm ³
	P ₂ O ₅	PbO	K ₂ O	MgO	BaO	CaO	V ₂ O ₅	Al ₂ O ₃	B ₂ O ₃					
A1	55.5	20.5	18.7	1.2	1.2	1.2	1.2	0.5	=	202	19.3	204	1.5819	3.27
A2	55	20.5	18.7	1.2	1.2	1.2	1.2	1	-	225	19.9	214	1.5829	3.31
A3	54.75	20.5	18.7	1.2	1.2	1.2	1.2	1.25	-	-	-	215	1.5848	3.37
A4	54.5	20.5	18.7	1.2	1.2	1.2	1.2	1.5	-	240	19.5	223	1.5830	3.36
A5	54.25	20.5	18.7	1.2	1.2	1.2	1.2	1.75	-	-	-	217	1.5839	3.29
A6	54	20.5	18.7	1.2	1.2	1.2	1.2	2	-	231	19.8	219	1.5867	3.27
A7	52	20.5	18.7	1.2	1.2	1.2	1.2	4	-	254	19.3	227	1.5864	3.24
A8	50	20.5	18.7	1.2	1.2	1.2	1.2	6	-	252	18.3	243	1.5955	3.25
A9	48	20.5	18.7	1.2	1.2	1.2	1.2	8	-	255	18.2	247	1.6081	-
B1	54	20.5	18.7	1.2	1.2	1.2	1.2	=	2	221	20.6	214	1.5819	3.27
B2	52	20.5	18.7	1.2	1.2	1.2	1.2	-	4	230	20.4	227	1.5840	3.26
B3	51	20.5	18.7	1.2	1.2	1.2	1.2	-	5	-	-	223	1.5867	3.24
B4	50	20.5	18.7	1.2	1.2	1.2	1.2	-	6	264	19.6	242	1.5889	3.48
B5	48	20.5	18.7	1.2	1.2	1.2	1.2	-	8	278	19.0	231	1.5887	3.37

Table 3. Glass compositions derived from glass PG III by substituting Nb₂O₅ for P₂O₅. The table contains also some physical property data.

glass	glass composition (in mol%)										$H_K 0.1/20$ in N/mm ²	n_D	ρ in g/cm ³
	P ₂ O ₅	PbO	Na ₂ O	MgO	BaO	CaO	V ₂ O ₅	Al ₂ O ₃	Nb ₂ O ₅				
N1	54.5	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0	270	1.5996	3.37	
N2	54.4	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0.1	276	1.5989	3.34	
N3	54.3	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0.2	267	1.6036	3.38	
N4	54.2	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0.3	272	1.5981	3.41	
N5	54.1	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0.4	269	1.6064	3.14	
N6	54.0	20.5	18.7	1.2	1.2	1.2	1.2	1.5	0.5	272	1.6037	3.39	
N7	53.5	20.5	18.7	1.2	1.2	1.2	1.2	1.5	1	264	1.6032	3.39	
N8	53.0	20.5	18.7	1.2	1.2	1.2	1.2	1.5	1.5	267	1.6036	3.34	
N9	52.5	20.5	18.7	1.2	1.2	1.2	1.2	1.5	2	-	1.6096	3.38	

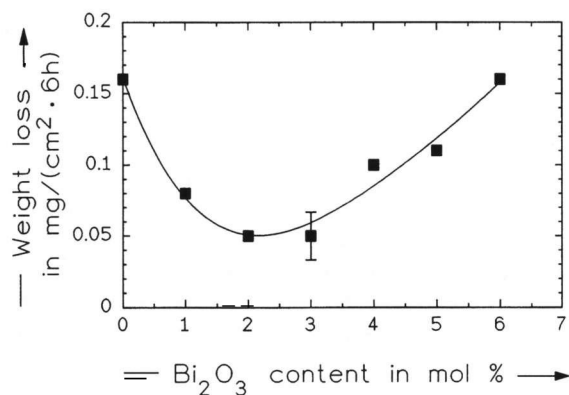


Figure 7. Water resistance of glasses at 60°C derived from glass PG III by equimolarly substituting Bi₂O₃ for Na₂O, PbO and P₂O₅, respectively.

and influences T_g , α , and the tendency to phase separation [13 and 14]. Earlier melting experiments demonstrated that in the case of phosphate glasses both the water content and the T_g value depend on the

melting time [1, 6 and 7]. Another problem with the preparation of phosphate glasses is the choice of a proper crucible material. Platinum crucibles are corroded strongly and one can expect that silica glass crucibles and even alumina crucibles are attacked to some extent, too. These questions need some further consideration.

Figure 8 shows that T_g of the glasses obtained depends considerably on the melting temperature between 610 and 925°C, whereas the melting time influences only moderately the glass transition. This melting interval was chosen, because it can be expected that below 600°C melting remains incompletely, and above 900°C volatilization of P₂O₅ increases measurably. Figure 9 shows that the chemical stability of the glasses also depends on melting conditions. A chemical analysis of the glasses gives evidence that SiO₂ contents of about 1 to 3% have been dissolved during the melting processes (figure 10). The other glass components were not influenced. In order to model the influence traces of SiO₂ may have on the chemical durability, glasses with the addition of up to 4 mol% SiO₂ were prepared. SiO₂

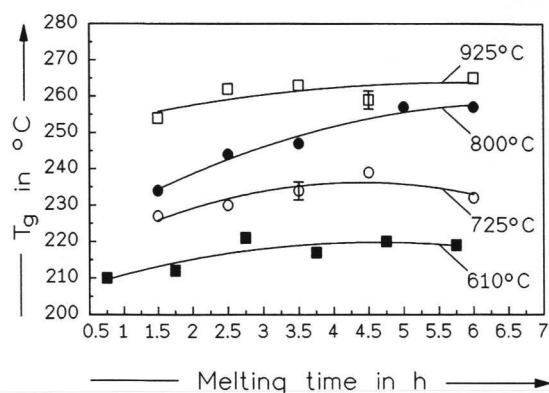


Figure 8. Influence of melting time and temperature on the glass transition temperature of glasses derived from glass PG IV.

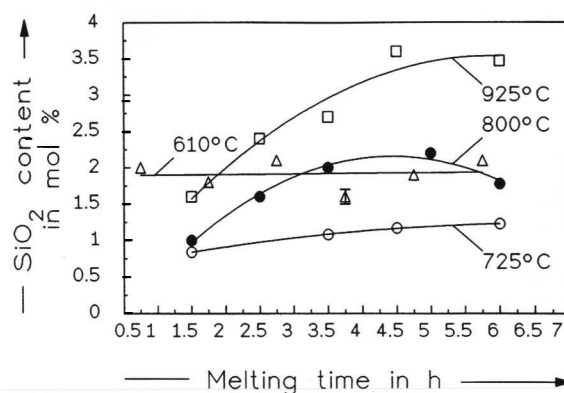


Figure 10. SiO_2 content of glasses from crucible corrosion as a function of melting time and temperature, glasses derived from glass PG IV.

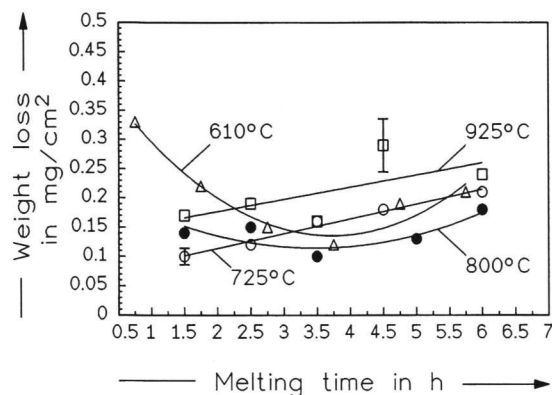


Figure 9. Water resistance of glasses at 60°C derived from glass PG IV as a function of melting time and temperature.

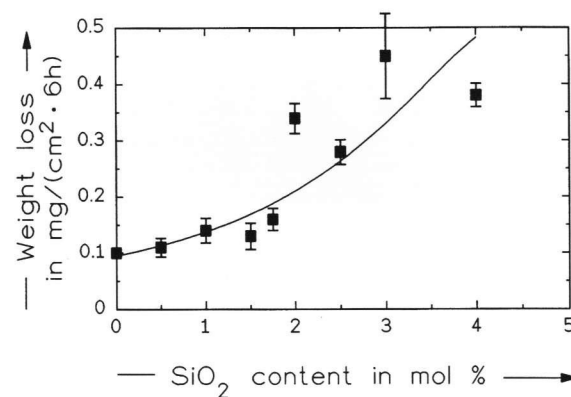


Figure 11. Water resistance of glasses at 60°C as a function of SiO_2 content, glasses derived from glass PG IV.

was added to the batch of glass PG IV and melted in a platinum crucible at 725°C for 1.5 h. The durabilities obtained are shown in figure 11. Within the error the thermal expansion coefficients of the glasses did not depend on the melting conditions.

3.4. Coating process

After having optimized the properties of the phosphate glass developed, coating trials were done. First, the coating of a plane fluoride glass by the phosphate glass was tried. After overcoming a lot of difficulties [17], an in-situ fiber coating could be performed. The corresponding experiments were done in cooperation with the Institut für Hochfrequenztechnik, Technische Universität Braunschweig (Germany). There a suitable rod-drawing equipment is available. Figure 12 displays a micrograph of a fracture surface. Although the fluoride fiber core still shows some defects like pores and crystals, the interface between the two materials and the

overclad is nearly perfect already. Experiments with a fluoride glass fiber core, a first fluoride glass coating and a final phosphate glass coating were also promising.

4. Discussion

The glasses developed are complex multicomponent substances. To a large extent the optimization processes described thus were of empirical nature. However, despite of some more or less trial and error experiments, several well-known glass structure principles were applied consequently, too. The first principle to be used is that of asking whether a component acts as a network former, as a network modifier or as an intermediate element. Coordination numbers, ionic radii and Dietzel field strengths are further important factors in this respect. Moreover, resulting from the nature of the chemical bond similarities and differences between silicate and phosphate structures have to be taken into account.

The main components of these glasses are P_2O_5 , PbO , and R_2O ($\text{R} = \text{lithium, sodium, potassium}$). P_2O_5 is the network former, and P_2O_5 and R_2O form alkali-phosphate chains which are cross-linked by PbO . Lead occupies also 4 fold-coordinated structure sites and



Figure 12. Optical micrograph of a fracture surface of fiber and overclad.

acts therefore like a network former [18 and 19]. MgO, BaO, CaO, and CdO are network modifiers with a stabilizing effect in the glass structure. The oxides V_2O_5 , WO_3 , Nb_2O_5 , B_2O_3 , Al_2O_3 and Bi_2O_3 are network formers or behave like these, at least under special conditions [18]. The final glass composition, which meets the demanded properties, i.e. chemical stability, thermal expansion, glass transition temperature and viscosity, has to be a compromise of all the different structural influences mentioned. Moreover, as has been shown, the melting conditions play also an important role, especially melting temperature, residual water content and the dissolved SiO_2 content from the crucible material have to be considered as real facts which influence the finally obtained properties. Structural factors and these more extrinsic dependencies have to be balanced.

Possibly the most important property in this respect is the chemical durability of these glasses. As shown, it is comparable to that of stable commercial soda-lime-silica glasses, at least in the short-time regime. For longer times a change in the dissolution mechanism occurs, however, the behavior of the chemical durability obtained here is fully sufficient for the present application. On the other hand, these phosphate-based systems have to be comparable to low- T_g , high-expansion fluoride glasses, e.g. those of the system ZrF_4 - BaF_2 - LaF_3 - AlF_3 - NaF . Such glasses are

“short” glasses what their viscosity-temperature dependence is concerned. Therefore, not only T_g of the phosphate glasses but also the viscosity at the fiberization temperature of the fluoride glasses is important. As the experiments showed the fluoride fiber drawing process including the phosphate glass overclad worked well. The drawing speed amounted to 5 to 7 m/min.

5. Conclusions

A glass system with low T_g ($<270^\circ C$) and high α ($>18 \cdot 10^{-6} K^{-1}$), matching to fluoride glasses, was developed to have a water resistance at $60^\circ C$ comparable to that of stable commercial container glasses. In the short-time regime its chemical stability was even not much worse than that of commercial borosilicate glasses. However, long-time experiments show lower stability of the phosphate glasses, possibly because of a different corrosion mechanism, compared to silicate glasses [20]. The main components of the glass were P_2O_5 , PbO, and Na_2O . However, further components like MgO, BaO, CaO, V_2O_5 , Al_2O_3 , and Bi_2O_3 , present in amounts ≤ 2 mol%, balanced the properties desired. Melting conditions like melting temperature and SiO_2 content from the crucible had to be considered, too. Fiber drawing experiments with an in-situ overclad of the fluoride glass fibers with the phosphate glass were successful.

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