SYNTHESIS OF FLUOROPHOSPHATE GLASSES WITH LOW MELTING TEMPERATURES

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ABSTRACT

Fluorophosphate glasses can combine low melting temperatures with a good chemical durability. In order to vary optical properties while retaining other features some new compositions were synthesized and some of their properties were investigated. The glasses were melted at 450 °C by using SnO, PbF_2, SnF_2, $NH_4H_2PO_4$ and NH_4PF_6 as raw materials. Metal fluorides like ZrF_4 and ZnF_2 were introduced, too. The T_g ranges between 87 and 141°C. Preliminary results concerning the transmission spectra in the UV, visible and medium IR range, the indices of refraction, and the densities are reported.

1. INTRODUCTION

Interest in fluorophosphate glasses developed from the combination of low melting temperatures, good chemical durability and desirable optical properties, such as a relatively high transmission in a broad spectral range, a high Abbe number and a wide range of the index of refraction. A carefully melted fluorophosphate glass exhibits ultraviolet transparency comparable to that of glasses based on BeF_2 and fused silica [1].
In spite of a significant interest in these glasses, few systematic studies on glass forming compositions and their properties have been reported. Therefore the objective of the present work

was to investigate glasses of various compositions in the PbF_2-SnF_2-SnO-P_2O_5 system and the effect of the addition of ZnF_2 or ZrF_4. The initial starting point was one of Tick's glasses [2] (glass I in table 1), which shows a very good resistance to water attack and has a low glass transition temperature T_g.

2. BATCH COMPOSITION

The basic batch composition (glass I) is covered by the system SnO-SnF_2-PbF_2-P_2O_5 (the batch mixtures are listed in table 1). The first step was to simply add ZrF_4 (glass II) to the original formula of Tick [2]. The next variation was to reduce the oxygen content by replacing SnO by the corresponding equimolar amount of SnF_2 and by adding increasing amounts of ZnF_2 (glasses III - V). A further increase of the fluorine content was tried by introducing NH_4PF_6 into the batch, the concentration of this compound ranged between 2.73 and 21.97 wt. % (glasses VI-VIII).

Table 1: Batch composition of the investigated glasses in wt %.

Batch	Glass							
	I	II	III	IV	V	VI	VII	VIII
SnF_2	30.70	30.27	58.08	57.28	56.51	57.28	48.62	45.93
SnO	26.43	26.04	-	-	-	-	-	-
PbF_2	6.75	6.65	6.38	6.30	6.20	6.30	5.34	5.05
$NH_4H_2PO_4$	36.12	35.60	34.16	33.69	33.24	33.69	28.60	27.05
NH_4PF_6	-	-	-	-	-	2.73	17.44	21.97
ZrF_4	-	1.44	-	-	-	-	-	-
ZnF_2	-	-	1.38	2.73	4.05	-	-	-

3. EXPERIMENTAL PROCEDURE

The glasses were melted in a 50 cm^3 vitreous carbon crucible using analytical grade raw materials. The crucible was placed into a muffle furnace at 450°C and heated for about 45 minutes. Due to the strong evaporation it was not possible to use a covered crucible. Clear fluid melts were obtained, which could readily be cast at room temperature into a brass mould.

The obtained transparent glasses were analyzed by X-ray diffraction (Cu Kα; glass plates of 4 x 5 cm^2 in size, thickness about 0.3 cm). The composition was determined by chemical analysis of F. Two glasses (glass II and VIII) were also analyzed with respect to P, Pb, Sn, and Zr; NH_x was analyzed qualitatively in glasses II and VIII; the oxygen content was not analyzed. The glass transformation temperature T_g was measured by differential scanning calorimetry (DSC) or differential thermal analysis (DTA) and the optical transmission by UV-, VIS-, and IR-spectroscopy of cast glass plates or powdered glass dispersed in KBr-pellets (IR). The index of refraction was determined by the immersion method and the density by applying Archimedes principle. A rough information of the chemical durability was obtained by leaching glass fragments in water at room temperature with subsequent balancing and optical control of the surface roughness.

4. RESULTS

4.1. GLASS FORMATION AND STRUCTURE

All batches yielded in clear glasses. Glass VIII was quite unstable and crystallized during storage in air. The X-ray diffraction diagramms of six glasses are shown in figure 1. Diffuse bands typical of vitreous materials can be seen. The intensity of the band at about 26° (2θ) differs a bit. Glasses II - VIII seem to have a higher degree of structural order than glass I.

4.2. COMPOSITION

Due to volatilisation the chemical analysis (tables 2 and 3) showed a severe loss of F of about 50 - 70 % with respect to the relative batch content. The highest F-content was achieved with batch VIII. Also Pb and P seem to form rather volatile components. The relatively high loss of Zr cannot be explained at the moment. NH_4^+ was qualitatively detected in the leaching solutions of both analyzed glasses. This indicates that NH_x-groups are still incorporated in the glass.

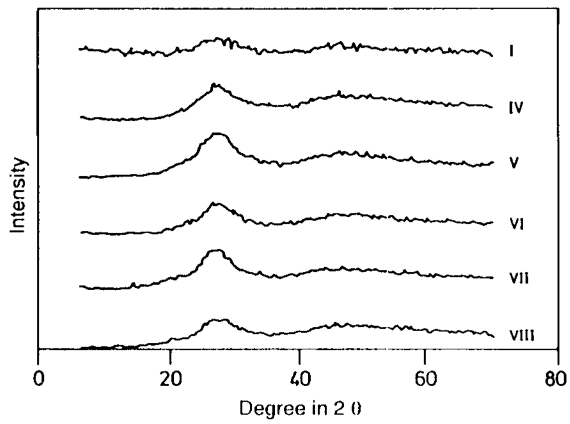

Figure 1: X-ray-diffractograms of glasses I and IV to VIII. The compositions are listed in table 1.

Table 2: Calculated elemental batch composition and chemical analysis of glass II and VIII in wt %.

Glass	II		VIII	
	calculated	analysed	calculated	analysed
F	8.94	4.4	27.12	11.8
P	9.59	9.2	11.42	11.9
Pb	5.63	5.2	4.26	5.6
Sn	45.69	55.3	34.68	52.4
Zr	0.75	0.3	-	-

4.3. TRANSFORMATION TEMPERATURE T_g AND DENSITY

The T_g (table 3) values vary between 87°C (glass VIII) and 141 °C (glass II) and decrease with the increasing fluorine content. The considerable increase of NH_4PF_6 in the batch (glasses VI - VIII) results in a significant decrease of T_g of about 30 K.
The glasses I and III - V have similar densities of about 3.91 - 3.96 $g \cdot cm^{-3}$, whereas the ZrF_4-containing glass II has the highest density of 4.05 $g \cdot cm^{-3}$. The addition of NH_4PF_6 leads to a significant decrease of the density (table 3).

Table 3: Transformation temperature T_g, density ρ, index of refraction n_D, and F-content of the glasses studied.

Glass	T_g/°C	ρ/g·cm^{-3}	n_D	F-content/wt. %
I	138	3.91	1.77	6.0
II	141	4.05	1.73	4.4
III	118	3.96	1.72	8.6
IV	108	3.94	1.72	8.7
V	107	3.96	1.73	9.1
VI	116	3.85	1.73	7.9
VII	90	3.61	1.69	9.4
VIII	87	3.52	-	11.8

4.4. OPTICAL TRANSMISSION AND INDEX OF REFRACTION

The prepared glasses have a good transparency in the visible and the near infrared. The UV cut off is at about 320 nm and is independant on the glass composition. In the normal IR range the glasses are transparent between 4000 and 1200 cm^{-1}. This indicates the absence of OH-groups. At about 1400 - 1600 cm^{-1} an absorption band is observed typical of NH-vibrations.

No remarkable differences were observed for any glasses. Figure 2 shows a transmission spectrum of glass VIII, typical of all the examined glasses.

The n_D values cannot be exactly correlated to the density (table 3), but they decrease with increasing F-content.

4.5. CHEMICAL DURABILITY

Glasses I and II showed no evident change after 1 hour in water but the surface of glasses III to VIII (tin oxide free batches) was strongly damaged after 1 hour. Similar tests in organic solvents like ethanol, acetone and dichloromethane showed no significant attack for any glasses.

5. CONCLUSIONS

On the basis of the glass system PbF_2-SnO-SnF_2-$NH_4H_2PO_4$ new glass compositions were realised using a melting procedure. The F-content was increased up to 11.8 wt. %.

The most important influence on the properties of the glasses results from the equimolar substitution of SnO by SnF_2 in the batch

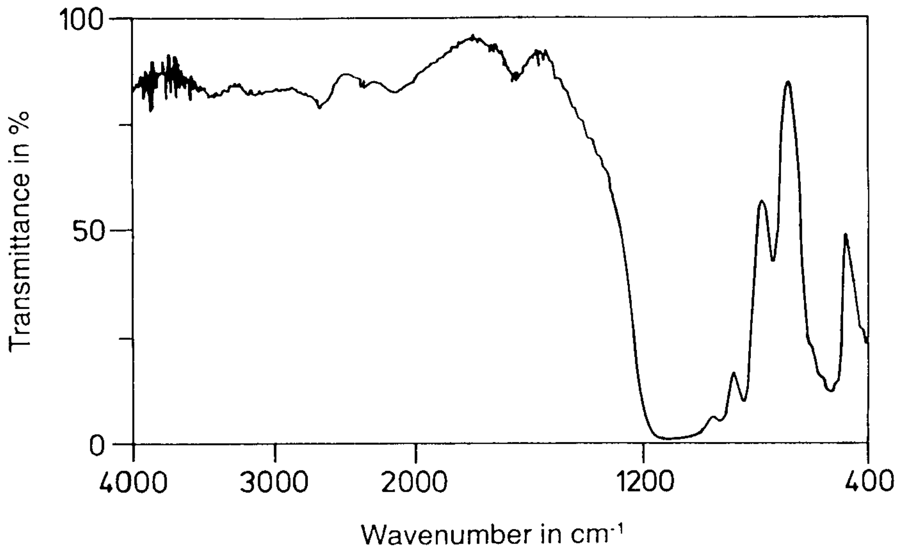

Figure 2: Transmission spectrum of glass IV in the IR range.

of glasses III - VIII. By this means the F-content is increased and the amount of metal-oxygen-bonds is probably reduced resulting in a decrease of T_g, density, and chemical durability. By further addition of fluorine by NH_4PF_6 the T_g decreases below 90°C. The incorporated NH_x-groups are leading to the formation of NH_4^+-ions in the leaching solutions. The structure of the incorporated nitrogen has not been investigated, but the content is considered to be responsible at least partially for the properties of these glasses.

6. REFERENCES

1) Cook L. and Mader K.: J. Am. Ceram. Soc. 1982, 45, 597.
2) Tick P. A.: Phys. and Chem. of Glasses 1984, 25, 149.