Formation, structure and properties of fluoro-sulfo-phosphate poly-anionic glasses

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ABSTRACT

Phosphate glasses exhibit high solubility for secondary anion species. This includes sulfate, fluoride or nitride ions, and enables the preparation of poly-anionic glasses. Here, we consider fluoro-sulfo-phosphates. We show that in this system, even equimolar anion mixing can be achieved without notably compromising the glass forming ability. The derived glasses exhibit surprising stability, what enables the fabrication of bulk samples mostly without the need to employ rapid quenching techniques. In terms of molecular structure, they rely on primarily ionic bonding among the different constituents, whereby the fluoride and sulfate anions seem to act as stabilizing ionic cross-linkers between highly-depolymerized phosphate entities. Investigation of the low-frequency Raman scattering indicates characteristic variations on intermediate-range structure, where a shift in the Boson peak appears to correlate inversely with increasing sulfate content. We discuss this observation in terms of the low level of bond localization and low field strength of the sulfate anion relative to phosphate Q^0 groups. Adjusting the degree of anion competition enables to tailor super-structural heterogeneity. Beyond this, the glass system provides an interesting variety of ligand situations for the potential incorporation of optically active cation species.

1. Introduction

Phosphate glasses count among the archetype classes of oxide glasses [1]. In a first consideration, they can be described through comparably straightforward and now well-validated structural models, where the constitutive building blocks of PO_4 tetrahedral units are interconnected across the oxygen corners. The degree of interconnection, often denoted as the degree of polymerization, depends on the presence of secondary cation species, i.e., the so-called network modifiers. For each positive modifier charge, one bridging oxygen species is transformed into a non-bridging (NBO) species, and there is only little disproportion. This picture follows Zachariasen's original network hypothesis [2] and has been evolving over the years to include more complex parameters on intermediate structural length scales [1,3–5], and non-linear interactions among cation species [6–9]. Specific interest arises from the presence of the one double-bonded oxygen in the PO_4 tetrahedron. The other three oxygen species are available for cross-linking, following the terminology of Q-groups in which the value of i in $Q^{i\,=\,0\ldots3}$ denotes the number of bridging oxygen species per phosphate

tetrahedron. When $i < 3$, the double-bond is delocalized. Polyphosphate glasses comprise of Q^3 and/or Q^2 units which form a network of crosslinked chains of PO_4 tetrahedra. An almost pure chain-structure is obtained in metaphosphate glasses, i.e., when there is exactly one positive modifier charge per PO_4. For higher content of modifier charges, the Q^2 chains become increasingly depolymerized until an ionic network of only Q^1 and Q^0 species is obtained. In such glasses, ionic crosslinking becomes the dominant structural parameter, which is why they are often called *invert* glasses. In particular for these, structural models are still evolving [10].

In terms of applications, phosphate glasses have been of significant interest as host material for rare earth ions (RE) [11–13]. This is due to the typically high solubility of virtually all RE species, the comparably low phonon energy which reduces non-radiative electronic relaxation in photoluminescence processes and, hence, potential use as laser gain medium. In addition, phosphate glasses usually provide a broader window of transparency as compared to silicate glasses, however, compromised by difficulties in controlling water content [14].

Interestingly, besides cation solubility, modification of invert

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phosphate glasses is possible also through anion substitution. For example, large amounts of SO_4^{2-} can be dissolved in zinc and other orthophosphate glasses, what significantly enhances glass forming ability and the material's thermo-chemical stability [15–20]. On the other side, fluorophosphate glasses incorporate significant amounts of fluoride species in a phosphate matrix. They have originally been designed for passive optics as well as laser applications so as to achieve high optical transmittance across the ultraviolet (UV) to near-infrared (NIR) spectral range, very low partial dispersion, and low linear and non-linear refractive index [21–24]. Further modification of the fluorophosphate anion network has been considered, e.g., through incorporation of P−N bonds [25], tellurite polyhedra [26], or sulfate groups [25,27], but usually with only minor degrees of substitution. More recent findings [28,29], however, suggest that this perceived limitation has been primarily due to the high melting temperatures which were employed in these previous studies [30], causing significant loss of sulfate through melt decomposition.

In the present report, we discuss formation, structure and properties of fluoro-sulfo-phosphate glasses across a broad range of sulfate and fluoride incorporation into meta- and orthophosphate matrices. While in these glasses, ionic interactions present the dominant structural parameter, surprisingly high glass forming ability and good glass stability are found. This demonstrates how anion-mixing presents an alternative route for tailoring the structural dynamics of phosphate invert glasses.

2. Experimental procedures

High purity (optical grade) raw materials of $NaPO_3$, AlF_3, Na_2SO_4, $Sr(PO_3)_2$, $SrSO_4$, MgF_2, CaF_2, SrF_2 were used for the preparation of $Na_2O\text{-}AlF_3\text{-}P_2O_5\text{-}SO_3$ (NAPFS) and $MgF_2\text{-}CaF_2\text{-}SrF_2\text{-}AlF_3\text{-}Sr(PO_3)_2\text{-}SrSO_4$ (FPS) glasses. The nominal compositions are given in Tables 1 and 4. Batches of 100 g were melted in Pt-crucibles, in a muffle furnace for 1.5 h at 850–1000 °C, followed by homogenization for 2 h at 1000–1100 °C (exact melting conditions are given in Tables 1, 4). FPS glasses with a phosphate-to-sulfate ratio ≥ 1 (D1–D3, E1–E3, F1–F3) and NAPFS were cast into preheated graphite moulds and annealed

(T_g + 50 °C) for 4 h before cooling to room temperature (RT) at a rate of about 3–5 K/h. Melts with a phosphate-to-sulfate ratio < 1 and sample A5 in the NAPFS series were rapidly quenched on a copper plate. These latter glasses were then similarly annealed from RT to T_g + 50 °C for 1 h, and cooled back to RT.

The density ρ of all glasses was determined with the Archimedes method at 25 °C in ethanol (NAPFS) or distilled water (FPS). Transition temperatures T_g were measured by differential scanning calorimetry (DSC, NETZSCH STA 449 F3 Jupiter equipped with DSC sample holders). Each measurement was done under inert atmosphere of N_2 with a controlled flow rate of 20 ml/min at a heating rate of 20 K/min. The value of T_g was extracted from the onset of the glass transition for each sample. In a similar way, the onset temperatures of crystallization were also determined by DSC, using a heating rate of 10 K/min and a home-built apparatus.

Vibrational spectroscopy (Raman and infrared) was conducted on polished samples with dimensions of 15x10x2 mm. High-frequency Raman spectra were collected over the spectral range of 50–1500 cm^{-1}, using an excitation wavelength of 514.5 nm in 90° scattering geometry on a Raman microscope. In addition, low-frequency Raman spectra were collected using a Renishaw InVia micro-Raman spectrometer equipped with a notch filter with performance down to ~9 cm^{-1}. For this, samples were similarly as with high-frequency Raman excited with a 514.5 nm Argon laser at ambient temperature, and the signal was collected on a CCD camera over the spectral range of 0 to 1375 cm^{-1} with a resolution of 2 cm^{-1}. Subsequently, empty scans were taken for the correction of air scattering at low frequencies. Data accumulation times varied between 90 s and 180 s, depending on the type of glass. For each sample, spectra were averaged over up to 10 scans. In the low-frequency region (10–200 cm^{-1}), Raman spectra of glasses typically exhibit an excess of vibrational density of states VDOS several times higher than the value predicted by the Debye model for an elastic continuum (which is a quadratic function of the frequency [31]). Such excess of vibrational density appears when plotting the reduced density of states $g(\omega)/\omega^2$ ($g_{Deb}(\omega) \approx \omega^2$) as a function of the excitation energy, and is manifested by a large asymmetric peak called "boson peak" with a maximum

Table 1

Physical and mechanical properties of the investigated NAPFS glasses: transition temperature T_g, density ρ, molar volume V_m, shear G, bulk K, Young's modulus E and Poisson ratio ν as well as atomic packing density C_g, volume density of bonding energy $< U_0/V_0 >$ and Young's modulus E, as calculated following the concept of Makishima and Mackenzie, [34] with nominal compositions (mol%) and synthesis conditions.

Series	Glass	Variable		Synthesis conditions (°C)	Thermal parameters (°C)			ρ (g/cm³)	V_m (cm³/mol)	G (GPa)	K (GPa)	E[a] (GPa)	E[b] (GPa)	C_g	$< U_0/V_0 >$ (kJ/cm³)	ν
					T_g	T_x	ΔT									
(100-x)NaPO₃-xAlF₃																
NAPF	A1	x	0	800, 1.5 h	289	–	–	2.500	40.79	14.3	29.4	36.9	31.5	0.522	30.19	0.29
	A2		10	850, 1.5 h	311	–	–	2.553	39.23	16.0	32.4	41.1	36.7	0.535	34.30	0.288
	A3		20	900, 1.5 h	325	–	–	2.616	37.61	18.5	36.0	47.3	42.3	0.55	38.42	0.281
	A4		30	1000, 1.5 h	367	–	–	2.682	36.01	22.2	41.1	56.5	48.1	0.566	42.54	0.271
	A5		40	1000, 1.5 h	412	–	–	2.753	34.42	28.3	46.5	70.5	54.4	0.583	46.66	0.247
(80-y)NaPO₃-20AlF₃-yNa₂SO₄																
NAPFS1	B1	y	0	900, 1.5 h	325	–	–	2.616	36.01	18.5	36.0	47.3	42.3	0.55	38.42	0.281
	B2		5	850, 1.5 h	327	–	–	2.725	36.83	20.8	39.8	53.2	44.3	0.573	38.60	0.277
	B3		10	850, 1.5 h	330	–	–	2.628	38.95	18.5	36.5	47.4	42.9	0.553	38.78	0.283
	B4		15	850, 1.5 h	314	–	–	2.624	39.78	17.3	35.6	44.7	43.1	0.553	38.97	0.291
	B5		20	850, 1.5 h	313	393	80	2.618	40.63	16.9	35.0	43.6	43.2	0.552	39.15	0.293
	B6		30	800, 1.5 h	288	323	35	2.631	41.96	–	–	–	–	–	–	–
70NaPO₃-(30-z)AlF₃-zNa₂SO₄																
NAPFS2	C1	z	0	1000, 1.5 h	367	–	–	2.682	36.01	22.2	41.1	56.5	48.1	0.566	42.54	0.271
	C2		5	850, 1.5 h	336	–	–	2.634	37.76	19.0	37.1	48.6	45.2	0.555	40.66	0.282
	C3		10	850, 1.5 h	330	–	–	2.628	38.96	18.5	36.5	47.4	42.9	0.553	38.78	0.283
	C4		15	850, 1.5 h	307	–	–	2.589	40.67	15.9	33.5	41.3	40.2	0.545	36.91	0.295
	C5		20	850, 1.5 h	298	366	68	2.559	42.27	15.5	32.5	40.1	37.7	0.538	35.03	0.294
Experimental error					± 2			± 0.002		± 0.1	± 0.6	± 0.7				± 0.003

[a] Determined by ultrasonic echography.

[b] Determined by the concept of Makishima and Mackenzie.