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Structure and properties of alkali and silver sulfophosphate glasses

Arnulf Thieme [a], Doris Möncke [a], René Limbach [a], Sindy Fuhrmann [a],
Efstratios I. Kamitsos [b], Lothar Wondraczek [a,*]

[a] Otto-Schott-Institute of Materials Research, Friedrich-Schiller-University of Jena, Fraunhoferstr. 6, 07743 Jena, Germany
[b] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constaniou Ave., 116 35 Athens, Greece

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ABSTRACT

Glasses of the composition 24 M_2SO_4-1 M_2O-52 ZnO-23 P_2O_5 with M═Li, Na, K, Rb, Cs, and Ag were prepared by conventional melt-quenching. Variation of the monovalent cation results in distinct changes in the thermo-physical, mechanical, and chemical properties. From Li to Cs, the calorimetric glass transition temperature and the stability against crystallization increase significantly. This trend is contrary to expectations in covalent glasses, but consistent with the behavior of ionic fluoride glasses. However, chemical and mechanical properties are consistent with the trend observed for covalent glasses as hardness and elastic modulus are drastically lowered from Li to Cs glasses. Modifier substitution with the heavier Ag ion has often similar effects as lithium substitution due to their comparably small coordination number (i.e., four) in the studied glasses. Raman- and IR-spectroscopic studies were carried out in order to correlate the variations in the glass properties with variations of the glass structure. Here, sulfate anions show preferential bonding to the monovalent cations while phosphate groups are preferentially linked to zinc-cations. For larger alkali cations the tetrahedral phosphate and sulfate groups show a reduction of symmetry, i.e., deviations from tetrahedral symmetry when acting as bi- or multi-dentate ligands.

1. Introduction

The class of sulfophosphate glasses, consisting only of sulfate and phosphate entities which are charge balanced by different metal cations, is still only partially investigated. These glasses were first described in connection with the vitrification of sulfatic waste in the 1980s [1–3]. The ternary system M_2SO_4–R_2O–P_2O_5 with M═Li and Na attracted interest for their ionic conductivity [4–7]. However, these types of glasses were not subjected to more intensive research for almost 30 years. Only recently, the Na_2SO_4–ZnO–P_2O_5 system (SP) was studied more systematically [8–15]. Such SP-glasses possess low softening temperatures around 330 °C [8], a high chemical stability compared to many phosphate glasses [11], and display a more brittle inelastic behavior and lower hardness with increasing sulfate load [12,16]. The glasses show also a high solubility for transition and noble metal ions [9,15,17] and were therefore studied regarding the formation and recovery of irradiation-induced defects [14,15]. Another interesting aspect of SP glasses is the fact that they represent a fully oxidic, though highly ionic glass system. For glasses with an S:P ratio of 1:2, the glass structure is entirely depolymerized, consisting of isolated sulfate and mono- as well as diphosphate anions, which are cross-linked by M^+ and M^{2+} ions [10]. In the hitherto studied glasses, Na^+ and Zn^{2+} cations are the basic constituents [8–15,17]. Recently we could show that as much as 35 mol% ZnO could be substituted by MnO in the SP system with a S:P ratio of 1:2 [17]. The present study explores the glass forming ability in this Na_2SO_4–ZnO–P_2O_5 system, where the monovalent sodium cation is systematically substituted along the alkaline group of the periodic table or with the pseudo alkaline silver ion. The glass matrix chosen for this study has a fixed S:P ratio of 1:2 to ensure a strong ionic character, and for the fact that so far no visible phase separation was observed. The properties of the synthesized glasses were systematically characterized and the structure was studied by vibrational spectroscopy. Changes in the glass properties of these strongly ionic oxide glasses are discussed in correlation to structural variations and the size, mass and coordination of the different monovalent cations.

2. Experimental

The basic nominal composition 24 M_2SO_4-1 M_2O-52 ZnO–23 P_2O_5 with M═Li, Na, K, Rb, Cs, and Ag (in mol%, M–SP) derives from the 24 Na_2SO_4-1 Na_2O-52 ZnO-23 P_2O_5 (Na–SP) glass system which we investigated in detail before [8–15,17]. The ZnO content remains fixed and the ratio of S:P is kept constant at 1:2. Only the monovalent Na ions of Na_2O and Na_2SO_4 were fully substituted by M^+ with M^+═Li^+, K^+, Rb^+, Cs^+ and Ag^+. The following analytic grade raw materials were used in glass preparation: $NH_4H_2PO_4$, ZnO, $ZnSO_4 \cdot 7H_2O$, Li_2SO_4, Na_2CO_3, K_2CO_3, RbCl, Cs_2CO_3, and Ag_2SO_4. For each composition 30 g test batches were prepared. A standard melting procedure was followed for most glasses [8,10,11]: calcination at 300 °C for 3 h, continuous

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* Corresponding author.
E-mail address: lothar.wondraczek@uni-jena.de (L. Wondraczek).

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temperature increase with ~3 K/min to 800 °C followed by fining at this temperature for 30 min. Most compounds were melted in gold crucibles (Na–SP, K–SP, Cs–SP). The glasses Ag–SP and Li–SP were prepared in corundum crucibles, at 800 °C, and the glass Rb–SP in a platinum crucible at a slightly elevated temperature of 850 °C. The melts were cast into pre-heated graphite molds (320 °C) and cooled down to room temperature (RT) with a rate of 30 K/h. X-ray diffraction (XRD) was carried out to prove the amorphous nature of the samples. Chemical analysis (scanning electron microscope/energy-dispersive X-ray spectroscopy, SEM-EDX) revealed minor dissolution and incorporation of Al_2O_3 from the crucible material (max. 0.5 mol%) in the Ag–SP glass. Quantitative results for all glasses are listed in Table 1.

Thermal properties of the synthesized glasses were characterized by differential scanning calorimetry DSC (Mettler Toledo DSC822e) in the range from 50 to 630 °C on powdered samples (20 mg), using a heating rate of 10 K/min. The chemical stability was gauged from changes in the optical transmission after treatment under autoclave conditions (2 bar, 119 °C, 95% rel. humidity) for 30 min. Optical transmission spectra of polished plane parallel sample plates, before and after chemical alteration, were obtained with a UV–Vis spectrometer (Shimadzu UV-3102PC, 190–3200 nm, error < 1%).

Infrared spectra were recorded in the specular reflectance mode from polished sample plates on an FTIR spectroscope (Bruker vertex80v, 25–4000 cm^{-1}, resolution 2 cm^{-1}). The reflectance data were treated by Kramers–Kronig transformation to extract the absorption coefficient spectra [18]. IR-absorption spectra were normalized in regard to the intensity of the phosphate band positioned at around 1100 cm^{-1}. Raman spectra were recorded in the 100–1400 cm^{-1} range on a micro-Raman spectrometer (inVia Renishaw) using the 488 nm line of an Ar ion-laser with a power of ~5 mW for excitation. Raman spectra were normalized to the intensity of the most intensive sulfate band, positioned around 1000 cm^{-1}.

The elastic properties were characterized by ultrasonic echography. The travel time of the longitudinal t_l and transversal echoes t_t was measured with an accuracy of ±1 ns by means of a piezoelectric transducer (Echometer 1077, Karl Deutsch GmbH & Co KG) with a center frequency ranging from 8 to 12 MHz. All measurements were performed on coplanar, optically polished specimens and their thickness d was determined using a micrometer screw with an accuracy of ±2 μm. On this basis, the longitudinal $v_l = 2d/t_l$ and transversal $v_t = 2d/t_t$ wave velocities were derived from the specimen thickness and the time between two consecutive echoes. The elastic constants, including the shear G, bulk K and elastic modulus E, as well as the Poisson ratio ν, were calculated by the following equations [19]:

$$G = \rho v_t^2 \tag{1}$$

$$K = \rho\left[v_l^2 - \frac{4}{3}v_t^2\right] \tag{2}$$

$$E = \rho\left[\frac{3v_l^2 - 4v_t^2}{(v_l/v_t)^2 - 1}\right] \tag{3}$$

$$\nu = \frac{v_l^2 - 2v_t^2}{2(v_l^2 - v_t^2)} \tag{4}$$

where ρ is the glass density. In addition, the mechanical properties were investigated by instrumented indentation testing with a nanoindenter (G200, Agilent Inc.), equipped with a three-sided Berkovich diamond tip and operating in the continuous stiffness measurement (CSM) mode. In this setup, the continuously increasing load–displacement signal is superimposed by a small oscillation of the indenter tip ($\Delta h = 2$ nm, $f = 45$ Hz). This enables the determination of hardness H and elastic modulus E as a function of the displacement into the surface by continuous recording of indentation depth, load and contact stiffness [16].

Table 1

Compositions of the prepared glasses with the nominal composition: 24 M_2SO_4-1 M_2O-52 ZnO-23 P_2O_5 or written as simple oxides: 19.8 R_2O-42.2 ZnO-19.1 SO_3-18.9 P_2O_5 (in mol%).

Glass	R_2O	ZnO	SO_3	P_2O_5	[a]	P:S	O:P
Ag–SP[b]	14.4 ± 0.3	45.5 ± 0.8	14.9 ± 1.0	24.6 ± 0.8	SEM	3.3	3.4
Li–SP*	21.6 ± 0.2	43.5 ± 0.4	16.6 ± 0.1	18.4 ± 0.2	ICP	2.2	3.8
Na–SP	16.1 ± 1.4	44.3 ± 3.2	18.0 ± 0.6	20.1 ± 0.6	SEM		
	19.2 ± 0.2	43.3 ± 0.6	17.3 ± 0.1	20.2 ± 0.2	ICP	2.3	3.6
K–SP	20.8 ± 0.8	39.9 ± 3.0	18.0 ± 0.7	19.3 ± 0.5	SEM		
	19.9 ± 0.2	41.8 ± 0.8	18.4 ± 0.1	19.9 ± 0.1	ICP	2.2	3.6
Rb–SP	11.7 ± 0.2	50.5 ± 0.2	17.7 ± 0.1	23.2 ± 0.1	ICP	2.6	3.5
	10.7 ± 0.3	51.9 ± 4.2	13.8 ± 0.7	22.9 ± 0.7	SEM		
Cs–SP	12.7 ± 1.2	42.4 ± 6.8	19.2 ± 1.7	25.7 ± 2.1	SEM	2.7	3.2

[a] Analyzed by SEM-EDX or by ICP-OES.

[b] Glasses contain to 0.5 mol% Al_2O_3 from the crucible (SEM).

On each glass sample, 15 indents as deep as 2 μm were generated at a constant strain-rate of 0.05 s^{-1} and with a 50 μm distance between each other to avoid the influence of residual stress fields [20]. Values of H and E were averaged between the upper 10% and the lower 20% of each indentation profile. All measurements were carried out in laboratory air under ambient conditions.

3. Results and discussion

3.1. Thermal, mechanical and chemical properties

Table 1 lists the analyzed compositions (by SEM-EDX) of the M–SP glasses which were obtained by normal melt-quenching for M═Li, Na, K, Rb, Cs and Ag with the nominal composition 24 M_2SO_4-1 M_2O-52 ZnO-23 P_2O_5 (in mol%). A small, though significant amount of sulfur (1–2 mol%) evaporates during the melting process. Compositional variations, especially the often low M_2O content in Table 1, might be explained by the underestimation of the alkaline elements by SEM-EDX analysis [21–23]. Other error sources can arise from variations in the water content of the raw materials, and thus, lower than expected batch fractions of the alkaline oxides. The O:P ratio in Table 1 denotes the degree of modification of phosphate units in the synthesized glasses. This ratio takes values of 3.0, 3.5 and 4.0 for meta- ($Q^2 = PO_3^-$), pyro- ($Q^1 = PO_{3.5}^{2-}$) and ortho-phosphate ($Q^0 = PO_4^{3-}$) units, respectively. Inspection of Table 1 shows that for glasses Ag–SP and Cs–SP the phosphate modification is slightly below pyro-phosphate, Rb–SP is exactly at the pyrophosphate composition, while Li–SP, Na–SP and K–SP are between the pyro- and ortho-phosphate compositions.

Selected glass properties are listed in Table 2. The glass density increases with the atomic weight of the monovalent ions from Li–SP to Cs–SP. Only the K–SP glass has an unexpected low density; however, this can be explained by the presence of small bubbles in this glass. The density of Ag–SP is larger than the density of Cs–SP even though the atomic weight of Ag is lower than the atomic weight of Cs. Comparison of the molar volume, V_m, shows a slight increase of V_m with increasing cation mass and increasing coordination number CN (for cation mass and CN values see Table 3). Interestingly, the value of V_m for Ag–SP falls between those of Li–SP (Li mass = 6.9 g/mol) and Na–SP (Na mass = 23 g/mol). Despite the Ag^+ ion's much higher molar mass (108 g/mol), it shares not only a low ionic radius but also a low coordination number (CN) with these two M^+ ions (see Table 3).

Thermal, mechanical and chemical properties of the SP glasses depend strongly on the respective glass composition, that is, the alkaline species. For example, comparison of the thermal properties reveals a systematic increase of the glass transition temperature from 285 °C to 348 °C in the series Ag < Li < Na < K < Rb < Cs (Table 1).

The DSC scans in Fig. 1 show for most glasses two distinct crystallization phenomena T_{XX1} and T_{XX2}. A two-step crystallization of sulfate (i.e. T_{XX1}) and phosphate phases (i.e. T_{XX2}) in Na–SP glass is induced by a microscopic phase separation [13]. Upon modifier substitution, a distinct