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Structural relaxation in $AgPO_3$ glass followed by *in situ* ionic conductivity measurements

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ABSTRACT

The structural relaxation kinetics of a silver meta-phosphate glass ($AgPO_3$) is investigated using a method based on the isothermal variation of its ionic conductivity over time. Samples of $AgPO_3$ glass from the same batch were pre-annealed at 433 K or 418 K and then relaxed at different temperatures within this temperature range, which is close to its glass transition temperature measured by differential scanning calorimetry, $T_g^{DSC} = 438$ K. Ionic conductivity data were continuously collected by impedance spectroscopy during the isothermal relaxation process. The variation of the electrical conductivity over time is well described by the Kohlrausch expression ($\Phi(t) = \exp[-(t/\tau_\sigma^K)^\beta]$), in which τ_σ^K is the characteristic relaxation time and β a stretch exponent. Different values of β were found when the glass structure expanded or contracted during relaxation. In addition, viscosity values calculated by the Maxwell relationship using $<\tau>$ from conductivity data and a shear modulus taken from the literature are in accordance with the experimental viscosity measured in the same temperature range, thus validating the use of ionic conductivity to unveil glass structural relaxation.

1. Introduction

Since glasses are out of thermodynamic equilibrium, their physical properties do not depend solely on the traditional thermodynamic variables such as pressure and temperature. Hence, at least one additional parameter is needed to define the degree of structural disorder of the frozen liquid. This additional parameter is the so-called fictive temperature (T_f). At this temperature, both the glass and metastable supercooled liquid would have the same structure.

When a glass is annealed long enough at a given temperature $T_{(1)}$ it reaches an equilibrium structure corresponding to that of the metastable liquid phase at this temperature. In this case, the fictive temperature of this material is $T_{f(1)} = T_{(1)}$. However, it is possible to change the fictive temperature if a new equilibrium state is reached at a different temperature $T_{f(2)}$. The structural change towards a new equilibrium state is called *structural relaxation*. During this structural relaxation process, all the properties that depend on the structure change over time.

Eq. (1) expresses the rate of an isothermal change for a given property during relaxation [1]:

$$\left(\frac{\partial P}{\partial t}\right)_{T,p} = -\frac{(P_t - P_\infty)}{\tau_P} \tag{1}$$

In this equation, P_t is the value of a property P at a time t, P_∞ is the value of P when equilibrium is reached, and τ_P is the relaxation time related to the investigated property. If τ_P is considered constant, and defining P_0 as the value of P at $t = 0$, the integration of (1) leads to the following relation:

$$\frac{P_t - P_\infty}{P_0 - P_\infty} = \Phi = exp\left[-\left(\frac{t}{\tau_P}\right)\right], \tag{2}$$

where Φ is the relaxation function, which is equal to zero when equilibrium is reached.

Note that if several parallel relaxation processes are possible, each having a specific relaxation time τ_P, Φ may be expressed by the Kohlrausch [2] expression, which is also known as the stretched exponential equation:

$$\Phi = exp\left[-\left(\frac{t}{\tau_P^K}\right)^\beta\right], \tag{3}$$

where $0 < \beta \le 1$, and τ_P^K is a characteristic relaxation time. The exponent β can be interpreted as a coefficient corresponding to a distribution of the relaxation time spectrum [3]. Note that if all the characteristic properties (*i.e.*, density, refractive index, conductivity…) are proportional to each other—which would be the case in a limited temperature range—this should lead to the same relaxation time, regardless of the property under study.

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In this work, the studied property (P) is ionic conductivity (σ) and the chosen glass is $AgPO_3$, whose glass transition temperature is low, $T_g^{DSC} = 438$ K, and whose ionic transport is due to Ag^+ cations [4]. Electrical conductivity measurements have been carried out to follow *in situ* the kinetics of the structural relaxation of an $AgPO_3$ glass. This technique allows one to obtain a large number of experimental data during the relaxation process, and consequently, well defined isothermal relaxation curves. However, this is not the case when the relaxation kinetics is determined based on the classical measurements of properties such as density [5,6] or refractive index [7] which are measured not continuously over time.

Therefore, the structural relaxation time τ_σ^K will be estimated in the temperature range of 418 to 433 K from variations in isothermal conductivity over time. Structural relaxation has already been detected using *in situ* complex impedance measurements in a window glass [8]. In addition, ionic conductivity has been applied to monitor structural relaxation in glassy pharmaceutical products [9] and also in the CKN glass [10].

As a consistency test, viscosity will be calculated using relaxation time from ionic conductivity and a shear modulus from the literature, both linked by the Maxwell fluid equation,

$$\eta = G{<}\tau{>}, \tag{4}$$

where the average relaxation time, $<\tau>$ is expressed by [1].

$$<\tau> \;= \frac{\tau_P^K}{\beta}\Gamma\left(\frac{1}{\beta}\right). \tag{5}$$

Thus, calculated values of viscosity will be compared with experimental viscosity data obtained in the same temperature range for the same batch of glassy $AgPO_3$. A discussion on the variation of β parameter is proposed.

2. Materials and methods

Glasses were prepared by melting and quenching an equimolar mixture of $AgNO_3$ and $NH_4H_2PO_4$ powders with purity over 99.5% from Sigma Aldrich. After 1 h of melting at 723 K in a borosilicate crucible (*Pyrex*®), drops of melt were splat-quenched at room temperature between two stainless steel plates. Several flat disk-shaped samples of transparent $AgPO_3$ glass with an average diameter of 8 mm and thickness of 1 mm were obtained from the same batch. The glass transition temperature ($T_g^{DSC} = 438$ K) was measured by differential scanning calorimetry at a heating rate of 10 K min^{-1} (DSC *Netzsch 404*).

For electrical conductivity measurements, gold electrodes were sputtered onto the two circular sides of the glassy samples prior to annealing, using a Quorum QR150 R ES Sputter. Conductivity was determined by impedance spectroscopy in a frequency range of 10 MHz to 5 Hz using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled to a Solartron 1296 Dielectric interface system. The samples were placed in a two-point sample holder and inserted in a Novotherm temperature control furnace, which provides temperature stability of ±0.1 K at the sample level. Impedance data were plotted in the complex plane plot, the so-called Nyquist diagram. The resistance (R) of the sample is thus obtained from the real axis location of the minimum of the opposite of imaginary part of impedance. Ionic conductivity (σ) is then calculated using the relation $\sigma = \frac{1}{R}\ \frac{l}{S}$ with l and S being sample's thickness and area respectively. Using this procedure, conductivity data were continuously collected *in situ* during the structural relaxation process, with over 20 data points per hour.

This *in situ* method ensures more precise results than intermittent measurements, such as density [5] or refractive index [6] as a function of time. These intermittent methods require samples to be cooled prior to measurement. We argue that this cooling step, which may introduce changes in the property under study, is obviated in the *in situ* method employed here.

In order to analyze samples with different fictive temperatures, one set of $AgPO_3$ glass samples was pre-annealed at 433 K (5 K below the T_g^{DSC}) for 24 h, and another set from the same batch, was pre-annealed at 418 K for 50 days. The purpose of this pre-annealing is to allow the glass to reach the structural equilibrium state at these two different temperatures, which will then be the initial glass fictive temperatures, $T_{f(1)}$.

Each glass sample was then inserted in the Novocontrol sample-holder, placed in the furnace, and the isothermal variations in their electrical conductivity were measured at different temperatures during the structural relaxation process of the glass. The furnace reaches the target temperature in less than 10 min. Note that a setup with high precision and high temperature stability is required for these measurements because of the relatively low variations in conductivity during the relaxation process when compared to the Arrhenius temperature dependence of the ionic conductivity of $AgPO_3$ glass. Thus, the accuracy of the experimental data is ensured by the thermal stability of the experimental setup (±0.1 K) and by the choice of the impedance spectroscopy technique used for conductivity measurements, eliminating resistance caused by electrode polarization.

The viscosity of $AgPO_3$ glass was measured at temperatures close to and below the T_g^{DSC} using a homemade penetration viscometer [11]. At a constant temperature, the penetration speed of a metallic rod in the glass enables one to determine the viscosity [12,13]. The penetration rod used here was a 1 mm diameter cylindrical stainless steel needle, and the temperature stability was ±1 K.

The conductivity and viscosity were measured in glass samples from the same batch. This was a necessary precaution because $AgPO_3$ glasses with the same nominal glass composition but different thermal histories may have different structures [14].

3. Results

Fig. 1 shows, as an example, the impedance complex plane plot obtained for the sample equilibrated at 433 K and measured at 428 K. Note that the resistance of the sample, read at the low frequency intercept of the semicircle with the real axis, increases with increasing time, thus the conductivity is decreasing.

Fig. 2 shows the isothermal conductivity variations as a function of time at 413, 418, 423, and 428 K of $AgPO_3$ samples pre-annealed

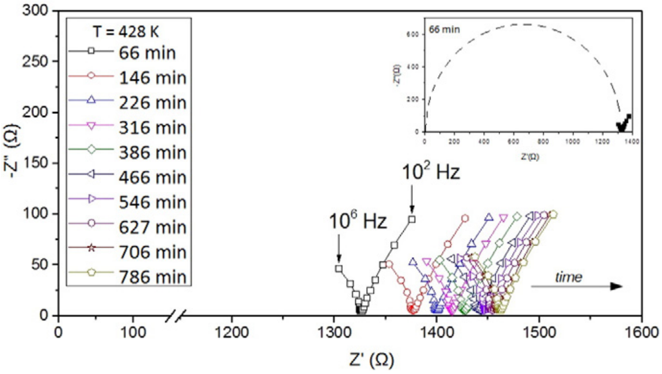

Fig. 1. Evolution with time of the complex plane plot of impedance data for $AgPO_3$ glassy sample pre-annealed at 433 K and relaxed at 428 K. Sample's resistance corresponds to the real part of impedance (Z') at the minimum value of the imaginary part ($-Z''$) and increases with time. For clarity, only selected data are shown. Sample's geometrical factor $l/S = 0.258$ cm^{-1} (l and S are, respectively, sample's thickness and area). Lines are guide to the eyes.