Journal of Non-Crystalline Solids 385 (2014) 9–16

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Behaviour of viscosity in metaphosphate glasses

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ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form 17 October 2013
Available online 17 November 2013

Keywords:
Phosphate glasses;
Viscosity;
Structure;
Nuclear magnetic resonance;
Raman spectroscopy

ABSTRACT

The experimental viscosity data of a series of alkali, alkaline earth and zinc metaphosphate glasses have been analysed using Vogel–Fulcher–Tamman, Avramov–Milchev and Mauro–Yue–Ellison–Gupta–Allan models. The kinetic fragility and activation energy for viscous flow have been obtained and studied as a function of the composition, paying special attention to the short and intermediate range order structure as studied by Nuclear Magnetic Resonance and Raman spectroscopy. The fragility shows an increasing tendency within the alkali and alkaline earth series and presents the lowest value for the $Zn(PO_3)_2$ composition. Meanwhile the modifiers influence on the local structure of the PO_4 tetrahedra follows a direct relationship with their cationic potential; both static Nuclear Magnetic Resonance and Raman experiments showed evidence of a change in the rings *versus* chains configurations at the medium range order that could have an important contribution on the variation of activation energy. Furthermore, the molar volume and average bond strength of the glasses have shown to play a most important role, having a similar variation as the activation energy in the high viscosity range. However, the low viscosity range data seem to increase with the modifier's cationic potential, thus suggesting a different flow mechanism when compared with the high viscosity range.

1. Introduction

Phosphate glasses have led to an extensive research field of glassy materials developed for a wide range of special applications. Their particular properties, low glass transition temperature, high thermal expansion coefficient and low optical dispersion compared with silicate glasses, allow phosphate glasses to be employed as low temperature glass to metal seals [1–4], high power lasers host materials [5,6], matrices for the vitrification of nuclear wastes [7] or bio-compatible materials [8].

The viscosity affects many aspects of glass manufacturing, such as melting and fining, devitrification, their forming and the efficiency of the internal stresses relaxation through annealing. During melting and glass forming processes, e.g. production of optical fibres, moulding of spherical lenses or glass to metal sealing, viscosity must always be kept under control to ensure high-quality products. However, the viscosity of phosphate glasses has been much less studied due to their lower and small-scale industrial production. The rapid variation of viscosity with temperature, as well as the pronounced devitrification tendency, may imply some difficulties to perform the measurements. As to our knowledge, few viscosity experimental data have been reported on phosphate glasses so far. There are several studies about how the thermal properties and the temperature dependence of viscosity are affected by the addition of metal oxides, such as Al_2O_3, ZnO, PbO or alkaline earth oxides to the batch composition [9–14]. The crosslinking of the metal cations between phosphate chains strengthens the glass network and influences not only glass properties but also help in improving the chemical durability. Structural relaxation studies have also been performed on phosphate glasses and its relationship with viscous flow [15–19]. Above the glass transition temperature, beam bending or micropenetration are those techniques commonly used to measure viscosity. At high temperature, the methods based on measuring the shear strain on the melt employing parallel plate, concentric cylinder, sinking bar or rotational viscometers, among others, are mainly utilize [9–19]. Oscillatory shear flow experiments are also employed to determine the complex dynamic shear viscosity (η^*) in the full range of temperature in order to study its dependence with time [20,21]. Also few experimental viscosity data belonging to publications up to 1985, mainly of binary alkaline and alkaline earth metaphosphate glasses measured by fibre elongation, are compiled in the handbook of glass data [22].

One of the most interesting features of a glass forming melt is its sharp increase of viscosity near the glass transition. In vitreous silica the variation of viscosity against the reduced temperature (T_g/T) can be approximated to an Arrhenius equation and constant activation energy of viscous flow can be determined [23]. In contrast, phosphate glasses present a much stronger variation of viscosity with temperature, thus referring to them as "fragile" glasses according to Angell's definition [24], while silicate glasses are classified as "strong". Therefore, for more fragile glasses, the viscosity variation with temperature can no longer be described by a single activation energy and the viscosity

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http://dx.doi.org/10.1016/j.jnoncrysol.2013.10.021

versus temperature dependence can only be analyzed with the help of empirical models, e.g. introducing the fragility parameter as in the Eq. (1) [24].

$$m = \left.\frac{\delta \log \eta(T)}{\delta\left(\frac{T_g}{T}\right)}\right]_{T=T_g} \tag{1}$$

In this work the temperature dependence of the viscosity in a series of metaphosphate glasses was evaluated using the three-parameter viscosity models that cover the full range of temperatures. Vogel–Fulcher–Tamman (VFT), Eq. (2) [25]:

$$\log \eta(T) = \log \eta_\infty + \frac{A}{T\text{-}T_0} \tag{2}$$

Avramov–Milchev (AM), Eq. (3) [26]:

$$\log \eta(T) = \log \eta_\infty + \left(\frac{\tau}{T}\right)^{\alpha} \tag{3}$$

and Mauro–Yuanzheng–Ellison–Gupta–Allan (MYEGA), Eq. (4) [27]:

$$\log \eta(T) = \log \eta_\infty + \frac{K}{T}\exp\left(\frac{C}{T}\right) \tag{4}$$

Some previous studies have also been carried out to study the relationship between the activation energy of viscous flow and the glass network structure in phosphate glasses [28,29]. Furthermore, Doremus proposed [30] another criterion for fragility based on the ratio of the activation energy of viscous flow at high (Q_H) and low viscosity ranges (Q_L) (Eq. (5)) for a number of oxide melts such as silica ($R_D = 1.38$), boron oxide ($R_D = 5.47$) or diopside melts ($R_D = 7.26$), but this has not been yet studied for phosphate glasses.

$$R_D = \frac{Q_H}{Q_L} \tag{5}$$

He found that viscosity presents, within the ranges of low and high temperature, an Arrhenius-type dependence, thus taking different values for the activation energy of viscous flow. By this evaluation of fragility, all the experimental viscosity data are involved in the analysis and not only those values near the glass transition temperature.

The aim of this work has been to get insight into the relationships between fragility, composition and structure of phosphate glasses, as determined by means of Nuclear Magnetic Resonance and Raman spectroscopy. A systematic study of the viscosity behavior in alkali, alkaline earth and zinc metaphosphate glasses has been carried out. The kinetic fragility of each glass has been determined by fitting the viscosity experimental data to the three models described above, and the activation energy of viscous flow, and its correlation with composition and structure, has been followed through the Doremus ratio.

2. Experimental

2.1. Glass melting

Alkali, alkaline earth and zinc metaphosphate glasses with compositions 50MO.50 P_2O_5 (M = Mg,Ca,Sr,Ba,Zn) and 50 $M'_2O.50P_2O_5$ (M' = Li,Na) were prepared by conventional melt-quenching procedure. Reagent grade raw materials analytically pure Na_2CO_3, MgO, $CaCO_3$ and ZnO (Panreac); $SrCO_3$ and $BaCO_3$ (Alfa Aesar); $(NH_4)_2HPO_4$ and Li_2CO_3 (Sharlau, ACS), were mixed and the batches were calcined in porcelain crucibles up to 450 °C, in a electric furnace, and then melted during 2 h at temperatures ranging from 900 °C to 1200 °C depending on composition. The melts were poured onto brass moulds and annealed slightly above their glass transition temperature.

2.2. Characterization of the glasses

Glass transition temperature (T_g), dilatometric softening temperature (T_d) and the Coefficient of Thermal Expansion (CTE) were determined from the thermal expansion curves of the glasses obtained in air with a *Netzsch Gerätebau* dilatometer, *model 402 PC/1* at a heating rate of 2 K min^{-1}. Prismatic samples around 10 mm in length were used for the measurements. The estimated errors in CTE and T_g are ± 2% and ± 1 K, respectively.

The density of the glasses was measured by helium pycnometry in a *Quantachrome Corp.* multipycnometer on bulk samples (±0.01 g cm^{-3}). The molar volume (V_m) of the glasses was calculated from density measurements by using the relation:

$$V_m = \frac{M}{d}\left(\text{in cm}^3\ \text{mol}^{-1}\right) \tag{6}$$

where M is the molar mass and d is the density of the glass.

The average single bond strength of binary glasses (B) could be expressed by the following equation according with the approach proposed in ref. [31], where $B_{M\text{-}O}$ is the corresponding single bond strength in each oxide and n_i is the molar fraction:

$$B = \sum(n_i B_{M\text{-}O})\left(\text{in}\,\frac{\text{kj}}{\text{mol}}\right) \tag{7}$$

Fourier Transformed Infrared (FT-IR) spectroscopy was performed on mirror-like polished glass samples around 2 mm in thickness in a *PerkinElmer Spectrum 100* spectrometer operating in the transmission mode within the wave number range of 950 to 5500 cm^{-1}. The water content of the metaphosphate glasses can be expressed in terms of the OH absorption coefficient (r_{OH}) that determines the relative concentration of OH in the glasses:

$$r_{OH} = \frac{-\log\frac{T_{3000}}{T_{5000}}}{l}\left(\text{in cm}^{-1}\right) \tag{8}$$

where T_{3000} and T_{5000} are the transmission at 3000 and 5000 cm^{-1} and l is the sample thickness (in cm). T_{5000} serves as a background transmission and includes the Fresnel reflection losses. To calculate the OH absolute content in ppm in the glasses the following equation is used:

$$\text{OH}_{\text{content}} = 30\,r_{OH}\left(\text{cm}^{-1}\right) \tag{9}$$

Magic Angle Spinning (MAS) ^{31}P Nuclear Magnetic Resonance (NMR) spectra were recorded on a *Bruker ASX 400* spectrometer operating at 161.96 MHz (9.4 T). The pulse length was 2.5 μs and 60 s delay time was used. A total number of 128 scans were accumulated with a spinning rate of 10 kHz. MAS NMR spectra were fitted to Gaussian functions, in accordance with the chemical shift distribution of the amorphous state. Solid (NH_4) H_2PO_4 was used as secondary reference with a chemical shift of 0.82 ppm with respect to H_3PO_4 (85%). The error in the determination of the chemical shift is taken as ±1 ppm.

Raman spectroscopy analyses were performed on a *WItec Alpha300RA* Raman-AFM confocal spectrometer with 532 nm laser wavelength excitation and 39 mW power in the range of 220–3800 cm^{-1}. The laser polarization angle was in x axis. Polished glass samples around 2 mm thick were used. The precision in the determination of the raman shifts is ±1 cm^{-1}.

The viscosity–temperature curves of the glasses were determined using the rotation and beam-bending methods at high and low temperature ranges, respectively. The viscosity of the melts in the range 10^3–10^1 dPa s was determined employing a high-temperature Haake viscometer of the cylindrical Searle type (Haake, Karlsruhe, Germany) equipped with a ME 1700 sensor. Rotation speeds of 3 to 15 rpm were used for 15 min, following the International Standard ISO 7884-2. Three