



Analysis of thermophysical properties of lead silicates in comparison to bulk metallic glasses

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ABSTRACT

The equilibrium viscosity and the specific heat capacity of three lead silicate glass forming liquids (flint glasses) with low glass transition temperatures are experimentally measured and compared to the thermophysical properties of network glass-formers like SiO₂ and GeO₂ and of bulk metallic glasses. The data are analyzed using the Vogel–Fulcher–Tammann (VFT) equation, the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) equation, and the Adam–Gibbs approach. The flint glasses depart from the Arrhenius equation in terms of liquid kinetics and their corresponding kinetic fragilities are intermediate between GeO₂ and the bulk metallic glass-formers. Among the lead silicates the fragility increases with increasing content of network modifiers, as lead, sodium and potassium modify the silicate network by creating non-bridging oxygen that softens the network.

1. Introduction

Glasses are liquids which have lost their ability to flow and behave as solids on the observation time scale. Every liquid can form a glass when crystallization is avoided, e.g. through rapid cooling. For this reason, glasses are found in every class of material and have a vast range of applications from standard window panels to high-end functional materials. Glasses can be formed by ionic bonded oxides with network-like structures, macromolecular materials as polymers and atomic glass formers like bulk metallic glasses (BMG). Lead silicate glasses (flint glasses) are oxidic network glass formers. Due to their high refraction indices, they are applied in optics. Optical properties, as any other property, depend on the relaxation state of the glass and therefore on the manufacturing process and the thermal history of the material. Among others the viscosity of a system has a tremendous influence on the manufacturing process and can change over several orders of magnitude within a relatively small temperature interval [1]. This temperature dependence varies significantly among different liquids. There are liquids that show Arrhenius-like temperature dependences of viscosity like SiO₂ and GeO₂ and liquids which deviate clearly from this behavior like *o*-terphenyl [2]. These differences in kinetics can be related to thermodynamic and structural differences of the glass forming systems. Regarding the thermodynamic properties, it is found that the kinetic behavior correlates with the height of the heat capacity change at the glass transition [3–5] and the temperature dependence of the excess entropy [2,6,7]. Furthermore, the kinetic fragility of glass-

formers must correlate with structural changes and efforts are made to quantify these correlations [8–11]. Altogether, these findings suggest strong connections between thermodynamics, structure and kinetics [12,13].

In this study, specific heat capacity and viscosity data of the flint glasses F2, LF5, and LLF1 are determined in the vicinity of the glass transition temperature, T_g , and compared to the network glass former GeO₂ and the metallic glass formers Mg₆₅Cu₂₅Y₁₀ and Pt₆₀Cu₁₆Co₂P₂₂. The differences in the properties of these materials are revealed and discussed in terms of correlations between structure, thermodynamics and kinetics.

2. Materials and methods

The flint glasses F2, LF5 and LLF1 were received from Schott AG. Their composition is shown in Table 1. The composition of the as-received material was confirmed by EDX measurements. The materials were slowly cooled with rates between $1.4 \times 10^{-4} - 5.6 \times 10^{-4} \text{ K s}^{-1}$ ($2-5 \text{ K h}^{-1}$) to obtain a deeply relaxed glassy state. F2, LF5 and LLF1 exhibit low glass transition temperatures of $T_g = 707 \text{ K}$, 692 K and 704 K [14], respectively, which are comparable to that of BMGs [13].

The viscosity of the glasses was measured using the three-point beam bending method as described for example in [15,16] using a Netzsch TMA 402 thermo-mechanical analyzer under a constant flux of dry air to prevent a possible reduction of the oxide glasses. Beams with rectangular cross-sections between 1.1 and 2.6 mm^2 and a length of

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Table 1
Composition in mol% of the three flint glasses LLF1, LF5, F2.

Composition in mol %	SiO ₂	PbO	K ₂ O	Na ₂ O	Network modifier
LLF1	80	8	6	6	20
LF5	72	12	6	10	28
F2	71	19	5	5	29

13 mm were centrally loaded by a fused silica pin. The viscosity can be determined from the deflection rate of the beam using the equation [17]

$$\eta = -\frac{gL^3}{144I_c v} \left(M + \frac{\rho AL}{1.6} \right) \quad (1)$$

where g is the gravitational acceleration, I_c is the cross-section moment of inertia, v is the mid-point deflection rate, M is the applied load, ρ is the density of the material. A is the cross-sectional area and L is the distance between the support points. The mid-point deflection rate is measured during isothermal annealing up to full equilibration to determine the equilibrium viscosity at the given temperature and during heating with a constant rate of 0.333 K s^{-1} . The viscosity relaxation of the material during the isothermal annealing is fitted with the Kohlrausch-Williams-Watts stretched exponential equation to determine the equilibrium viscosity

$$\eta(T) = \eta_i - \eta_{eq-i} \left\{ 1 - \exp \left[-\left(\frac{t}{\tau} \right)^\beta \right] \right\} \quad (2)$$

where η_i is the initial viscosity when reaching the isothermal temperature. η_{eq-i} is the difference between the initial viscosity and the equilibrium viscosity, which the material is approaching. τ is the relaxation time for the equilibration and β is the shape parameter. The equilibrium viscosity is given by $\eta_{eq} = \eta_i + \eta_{eq-i}$.

The specific heat capacity is measured by means of differential scanning calorimetry (DSC) against a sapphire reference with a step method [18] in a power-compensated Perkin Elmer Hyper-DSC 8500. The temperature is increased by 10 K with a rate of 0.33 K s^{-1} from the start temperature and then held isothermally. This leads to a peak in the heat flow signal, whose height is proportional to the power which is needed to heat the sample for 10 K. To eliminate the influence of the sample and to relate the heat capacity to a reference the step method is applied using an empty pan, the sample and a sapphire reference as well. Fig. 1 shows the heat flow signal of a single step in the protocol for an empty pan, a LF5 sample and the sapphire reference. Upon heating from T_{Start} to T_{End} , the heat flow signals show maxima. From the maxima in the three consecutive measurements the heat capacity of the sample can be calculated by the equation

$$C_p^{\text{sample}}(T) = \frac{\dot{Q}_{\text{sample}} - \dot{Q}_{\text{pan}}}{\dot{Q}_{\text{sapphire}} - \dot{Q}_{\text{pan}}} \frac{m_{\text{sapphire}} \mu_{\text{sample}}}{m_{\text{sample}} \mu_{\text{sapphire}}} C_p^{\text{sapphire}}(T) \quad (3)$$

according to [18,19], where \dot{Q}_{sample} , \dot{Q}_{pan} and $\dot{Q}_{\text{sapphire}}$ are the heat flow of sample, pan and sapphire. m_{sample} and m_{sapphire} are the mass of the sample and sapphire specimen and μ_{sample} and μ_{sapphire} are the molar weight of the sample material and sapphire. $C_p^{\text{sapphire}}(T)$ is the specific heat capacity of sapphire. This procedure is repeated every 10 K to obtain specific heat capacity values with a step size of 10 K. It is important to note that the isothermal holding between the heating steps must be long enough to equilibrate the thermal signal of the sample. To ensure this, the samples were held isothermally for 120 s after each heating step.

The specific heat capacity data in the glassy state are modeled with the equation described by Inaba et al. [20,21] as

$$C_p^{\text{glass}}(T) = \frac{3R}{M} \left[1 - \exp \left(\frac{-1.5T}{\theta_D} \right) \right] \quad (4)$$

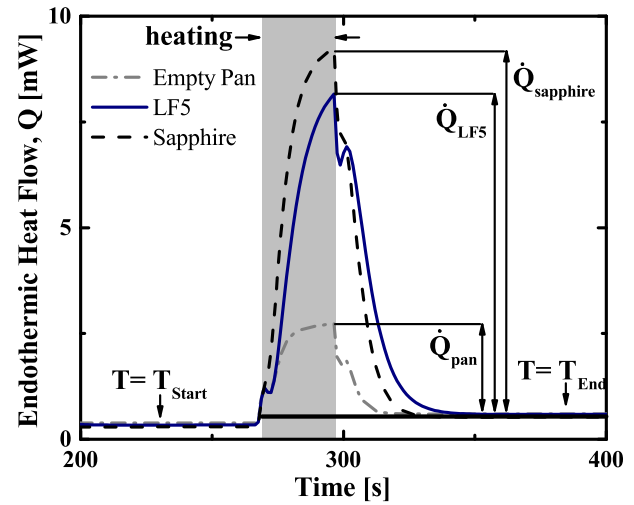


Fig. 1. Endothermic heat flow of empty pan (grey, dash dotted line), LF5 (blue, solid line) and sapphire (black, dashed line). Upon heating from T_{Start} to T_{End} the heat flow exhibits a maximum. The specific heat capacity at T_{End} is calculated from the maxima of the heat flow using Eq. 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this equation, M and the Debye temperature, θ_D , are kept as fitting parameters, R is the universal gas constant, and T is the absolute temperature. The specific heat capacity data in the liquid is fitted using Kubaschewski's equation [22]:

$$C_p^{\text{liquid}}(T) = 3R + aT + bT^{-2} \quad (5)$$

with a and b being fitting parameters.

3. Theory

3.1. Structure

Pure SiO_2 and GeO_2 are the archetypical network glass formers, which build a rigid network of SiO_4 and GeO_4 tetrahedrons [23]. Flint glasses like F2, LF5 and LLF1 are also network glass formers, in which the main constituent SiO_2 is the backbone of the oxide network, which is formed by SiO_4 tetrahedrons. PbO can be a network modifier at concentrations below 25 mol% or a network former at higher concentrations. In the case of F2, LF5 and LLF1, it is a network modifier like Na_2O and K_2O , which increases the number of non-bridging oxygen atoms within the network [24–28]. As LLF1 has the lowest and F2 the highest content of network modifiers, the rigidity of the network should decrease from LLF1 to F2, as more and more non-bridging atoms and free ends exist in the network. Like oxide glass formers, BMGs arrange in clusters on the nearest neighbor length scale [29,30], but due to the unidirectional, weaker metallic bonding, the structure of BMGs is less rigid than in network glass formers.

3.2. Kinetics

The glass transition at the temperature T_g is a kinetic event, which occurs when the liquid loses its ability to flow and freezes to a glass. For conventional slow to intermediate cooling rates, the viscosity of a liquid reaches a value of about 10^{12} Pa s at T_g . The kinetics of a glass-forming liquid is reflected by the temperature dependence of its viscosity, which varies significantly among glass forming liquids. Following the fragility concept of Angell [31], liquids with a steep temperature dependence of viscosity (η) at T_g and therefore with a large deviation from Arrhenius-like behavior are considered as kinetically “fragile”. On the contrary, liquids with an Arrhenius-like temperature dependence are kinetically “strong” liquids. To quantify the fragility, the slope of the viscosity

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