

Technical note

Viscosity of high-nitrogen content Ca–Si–O–N glasses

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Abstract

The viscosity of three high-nitrogen content Ca–Si–O–N glasses, with 30–58 e/o N and 36–39 e/o Ca, was determined by micro-indentation. The measurements were made using an automated set-up, designed and built in-house, capable of measurements up to 1200 °C with applied loads of 0.01–15 N. The viscosity increases significantly with the nitrogen content and reaches viscosity values close to reported values for rare-earth silica oxynitride glasses. The glass transition temperatures range between 878 and 995 °C and are in very good agreement with values measured by differential thermal analysis. The apparent viscosity activation energies are very high, ranging from 855 to 2170 kJ/mol. The glasses can accordingly be classified as being both very refractory and very fragile. Implications of the viscosity values and mechanical properties of the glasses for their structures are discussed.

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Oxynitride silicate glasses have been the subject of many studies since the late 70s, from both scientific and technological points of view, at which time it was realized that incorporation of nitrogen into silicate glasses markedly alters mechanical properties such as strength, toughness, elastic moduli, and hardness,^{1–6} glass transition temperatures and thermal expansion coefficients.⁷

Oxynitride glasses have traditionally been synthesized by melting mixtures of glass modifier metal oxides, SiO₂ and Si₃N₄, yielding glasses with nitrogen contents up to typically *ca.* 30 e/o (N content in e/o = 3[N]/(3[N] + 2[O]), with [N] and [O] the atomic concentrations of N and O, respectively). However, an alternative synthesis method developed by us has enabled the preparation of oxynitride glasses with significantly higher concentrations of nitrogen, as well as modifier additives, in various systems.^{8–11} In the synthesis route, the modifier is introduced as a metal or metal hydride, which reacts with nitrogen gas at relatively low temperatures and forms reactive nitrides with no surface oxide layer. These glasses retain high amounts of the electropositive elements and nitrogen and exhibit very high

values of glass transition temperatures, microhardness, elastic moduli and refractive index. The present Ca–Si–O–N glasses were prepared by using this synthesis method.

In comparison with other physical properties the influence of the nitrogen content on the viscosity of oxynitride glasses has been little studied so far. In all cases it is found that the viscosity significantly increases with increasing nitrogen content. Glass systems that have been investigated with regard to viscosity are Y–Al–Si–O–N^{1,12,13} and M–Si–Al–O–N¹⁴ with M = Mg, Ca, Y, Nd. The yttrium containing glasses show, for similar nitrogen contents, higher viscosity values than the glasses containing Mg, Ca and Nd. Nonetheless, no study shows clear evidences of a change in apparent activation energies for viscous flow correlated to the nitrogen content.

The Ca–Si–O–N were prepared from mixtures of CaH₂ (98% with Mg < 1%, Alfa Aesar GmbH & Co.), Si₃N₄ (ChemPur GmbH), and SiO₂ (99.9%, ABCR GmbH & Co.) powders. The powders were stored and handled in a glove box under Ar atmosphere to avoid exposure to air. Six-gram batches for each composition were grinded, pressed into pellets, and placed in niobium crucibles that were covered with parafilm for avoiding air contact during the transfer from the glove box to the furnace. The mixtures were melted in Nb crucibles at 1500–1750 °C using a radio frequency furnace. Details con-

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Table 1
Physical properties of the glasses – Vickers hardness (Hv) values were measured with a 500 g load¹¹; Young's and shear elastic moduli, E and G , were measured by means of ultrasonic echography¹⁵ or calculated.¹⁵

Glass grade	Glass composition	N/e/o	Ca/e/o	n_{BO}	ρ g cm ⁻³	T_g , °C determined by DTA ± 5 °C	T_g , °C from viscosity measurements	Hv, GPa	E , GPa	G , GPa	ν^a
N 30 e/o	Ca _{11.88} Si ₁₀ O _{22.06} N _{6.50}	30.7	37.1	3.26	3.13	887	878 \pm 5	7.73	–	–	–
N 36 e/o	Ca _{12.90} Si ₁₀ O _{20.93} N _{7.98}	36.4	39.2	3.22	3.02	912	896 \pm 9	7.75	110	43.4	0.30
N 58 e/o	Ca _{11.04} Si ₁₀ O _{13.21} N _{11.8}	58	35.6	3.29	3.24	1010	995 \pm 5	9.62	135	52.8	0.28

^a Poisson's ratio (ν) is calculated by means of the classical relationship: $\nu = E/(2G) - 1$.

cerning synthesis and additional characterisations are given in Refs.^{9,10}

The amorphous nature of the glasses was verified by X-ray powder diffraction, using a Guinier–Hägg camera and Cu $K\alpha_1$ radiation. Cation concentrations were determined by energy dispersive X-ray point analysis and anion contents determined by combustion analysis (LECO equipment). Measured physical properties for the three Ca–Si–O–N glasses are given in Table 1.^{11,15} In this table, the number of bridging anions per tetrahedron (n_{BO}^*) was roughly estimated assuming all silicon atoms are 4-fold coordinated to anionic species and all anions are bonded to cationic species. This number is defined as: $n_{BO}^* = 4 - \sum_i M_i z_i / (\sum_j F_j)$ where M_i and z_i are the atomic fraction and the valency of the i th modifying cation and F_j is the fraction of the j th glass forming cation.

Owing to the used synthesis method or difficulties in synthesis, the volume of obtained glass specimens is typically less than 1 cm³ and, in these conditions, instrumented indentation is among the most powerful methods (maybe the only one) to assess rheological properties. The shear viscosity coefficient (η) was estimated using an home-made equipment operating in the micro-indentation range (see Refs.^{16,17} for details), under a constant load of 10–12.5 N in air at temperatures between 870 and 1030 °C, using a ball sapphire indenter (750 μ m radius). The expression for the creep compliance ($J(t)$) derives from the general solution for the condition of a contact between a rigid indenter and a viscoelastic material with a linear behaviour^{18,19}:

$$J(t) = \frac{8\sqrt{R}}{3(1-\nu)P} u^{3/2}(t) \quad (1)$$

Assuming that for a long duration the viscous contribution to the total penetration greatly predominates over the other ones, it leads to $(1/\eta) = \lim_{t \rightarrow +\infty} (d/dt)J(t)$. In the expression of $J(t)$ in Eq. 1, Poisson's ratio is assumed to be constant: $\nu = 1/2$, assuming that glass is incompressible in the transition range. For the measurements of this study, the load was maintained long enough to insure the occurrence of a stationary creep regime, as evidenced by a constant slope in the $u^{3/2}/P$ versus t curves, as shown in Fig. 1.

Viscosity data are plotted as a function of the reciprocal temperature in Fig. 2. The glass transition ranges conventionally associated to a η between 10¹² and 10^{12.6} Pa s are in the 878–995 °C interval (Table 1) and are in excellent agreement with those previously determined by DTA^{10,22} (Table 1). Moreover, both measurements show a linear increase of glass

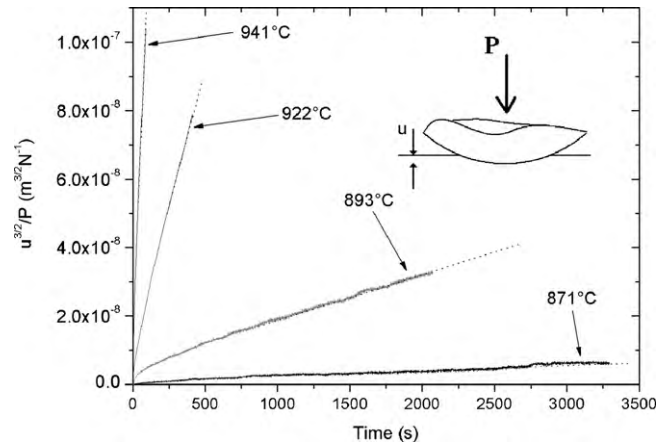


Fig. 1. Typical indentation creep curves, for the N 30 e/o grade.

transition with e/o N (4.44 ± 0.07 K per e/o N). This is consistent with the observation of Hampshire et al.^{1,20} and Dolekcecik et al.²¹ who observed a linear increase of the glass transition in the Ca-, Mg-, Nd- and Y–Si–Al–O–N systems with e/o N (almost 3–4 K per e/o N). It illustrates that this linear dependence is also effective for very high e/o N.

The viscosity values for the Ca–Si–O–N glasses, increasing significantly with increasing nitrogen content, are consistent with previously reported values for oxynitride silicate glasses with comparable nitrogen contents^{13,22,23} and with the viscosities reported by Hampshire et al.¹⁴ in the case of Mg–Si–Al–O–N and Ca–Si–Al–O–N glasses, with viscosities

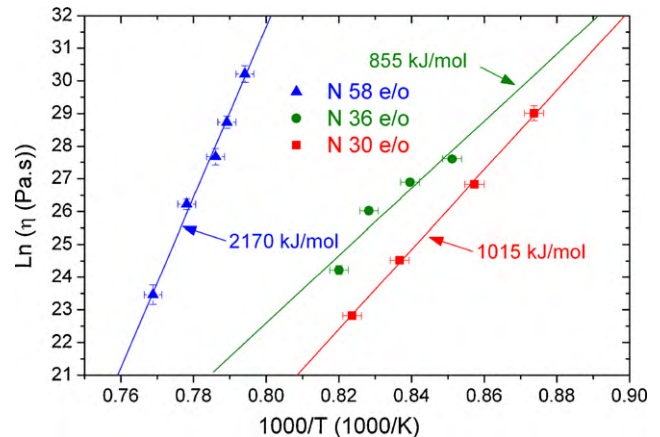


Fig. 2. Logarithm of the viscosity of Ca–Si–O–N glasses as a function of reciprocal temperature. The full lines correspond to the Arrhenius expression for viscosity.

of 10^{14} and 10^{13} Pa s at 860 and 890 °C, respectively, for a Ca glass with 18 e/o N. In addition, the glass viscosity was found to increase with decreasing the size and increasing the field strength of the modifier ions.²³

The temperature dependence of η can be nicely described by an Arrhenius-type law $\eta = \eta_0 \exp(Q/RT)$ (Fig. 2), where Q is the apparent activation energies for viscous flow. The heat for flow derived from temperature jump experiences using this expression are remarkably high and range between 855 and 2170 kJ/mol. Values of the order of 1000 kJ/mol have previously been reported for silica oxynitride glasses.^{13,23} Note that we cannot conclude that Q changes from 30 to 36 e/o N, because of the large uncertainty regarding the apparent activation energy for flow of the 36 e/o N composition.

There have been only a few reports on the viscosity of oxynitride glasses containing alkaline earth elements and, to our knowledge, none for Ca–Si–O–N glasses. Previous studies^{23,24} have demonstrated that the viscosity of oxynitride glasses increases with increasing nitrogen content, because increasing the nitrogen content increases the polymerization degree, but do not evidence a large increase of the apparent activation energy. Nitrogen is assumed to be 3-fold coordinated to silicon in oxynitride glasses and is therefore expected to increase the glass network polymerization. The substitution of O by N in oxynitride glasses is now well admitted. NMR studies²⁵ suggest that N-rich La–Si–O–N glasses (>50 at.%) are dominated by SiO_2N_2 interconnected tetrahedron, and $Q^1(\text{O}_4)$, SiO_3N and SiON_3 units also exist, so tetrahedron with up to 3 non-bridging anions, but no $Q^2(\text{O}_4)$ units are detected.

The presently studied glasses also contain high amounts of modifier elements and it is likely that these cations play an important role on the glass network structure and on the physical properties. The high-nitrogen content M–Si–O–N (M = La, Sr, Ca) glasses^{8–10} have determined compositions with X:Si ([O,N]/[Si]) ratios that are high, ranging up to 3 and even above so that a significant fraction of anions are non-bridging (there are 4 bridging anions per silicon tetrahedron at maximum, i.e. non-bridging ions show up when X:Si ratio becomes larger than 2), and the average network polymerization degree is relatively low and the networks is “fragmented”. The average network connectivity of N-rich La–Si–O–N glasses X:Si suggests that atomic network consists of network made of small rings and/or chains.⁸ The X:Si ratio in Ca–Si–O–N¹⁰ (>2.4) indicates that such fragmented network also exists for this system. It results in structural heterogeneities at the atomic or molecular scale.

For the present Ca–Si–O–N glasses, it is interesting that although they show high T_g temperatures, typically above 890 °C for nitrogen contents above 30 e/o, they also exhibit large values for the activation energy for viscous flow. In other words, following the concepts of fragile and strong glasses,²⁶ they are simultaneously very refractory (nearly as refractory as a-SiO₂ for the glass with 58 e/o N) and extremely fragile ($Q > 2000$ kJ mol⁻¹).

It is difficult to explain the high temperature sensitivity of the viscosity for the present Ca–Si–O–N glasses. It is supposed that increasing the polymerization degree decreases the Poisson's ratio²⁷ and increases the atomic packing density. For example,

with four bridging oxygen atoms per tetrahedron a-SiO₂ exhibits a Poisson's ratio of ≈ 0.15 , whereas for alkali-alkaline-earth-silicate glasses $\nu > 0.2$. The nitrogen content induces indeed an increase of the atomic packing density.^{15,28,29} But, even if high e/o N induce high Poisson's ratio – up to 0.29 for the glass with 42 e/o N – the Poisson's ratio is largely controlled by the cation modifier contents. As the cation modifier content increases, the Poisson ratio increases¹⁵ (almost linearly, from 0.276 for 33.2 e/o Ca to 0.291 for 38.0 e/o Ca). So, the increase of Poisson's ratio with e/o Ca confirms that high cation modifier content induces a depolymerization and a fragmented network.

The seemingly atypical behavior of oxynitride glasses regarding their viscosity-temperature dependence and the nitrogen incidence upon the atomic packing density can be tentatively explained on the basis of an heterogeneous atomic network, with a segregation of nitrogen into highly polymerized and relatively rigid regions that are surrounded by “softer” and less refractory regions, i.e. clusters embedded in a less viscous matrix. On one side, the matrix would favour a high packing density by allowing for atomic or molecular displacement. On the other side, it would be responsible for the strong temperature sensitivity of the viscosity – or fragility. The glass structure would accordingly contain weak channels, resembling the ones proposed by Greaves³⁰ for high cation modifier contents and acting as a lubricant between the clusters.

This calls for further structural investigations in these still rather exotic and poorly understood glasses.

Some exploratory TEM investigations were performed on Ca–Si–O–N glasses,²⁵ but did not reveal any heterogeneity. Selected area electron diffraction patterns were also unable to evidence any crystallites or any phase separation. SEM analysis leads to the same conclusions.¹⁰ However, TEM analysis on N-rich La–Si–Al–O–N possibly indicates a phase separation in a length-scale of 5 to 10 nm in both La–Si–Al–O–N and La–Si–O–N glasses. But we cannot exclude an effect of sample thickness variation during measurement.²⁵ This clearly calls for further investigations. However, the presently determined apparent activation energy for flow, which is 2–3 times larger than those of silicates glasses (oxides), suggests some heterogeneities at the sub-micron scale.

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