

MECHANICAL STRENGTH AND VISCOELASTIC PROPERTIES OF FUSED SILICA: THE ROLE OF DEFECTS

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ABSTRACT

Many of the anomalous properties of fused silica (e.g. small or negative thermal expansion and anomalous temperature and pressure coefficients of elastic constants), can be explained simply by a consideration of its open, 3 dimensional, fully coordinated structure, with no reference to point defects. The mechanical strength may also be discussed without concern for such defects, although recent work suggests that they have a role. On the other hand, the involvement of defects seems necessary to explain both viscous flow and delayed elasticity.

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I. INTRODUCTION

The lack of structural and mathematical tools to quantitatively describe the randomness of their structure makes an understanding of the structure and thus structure/property relations in glasses difficult. As a result, we must (1) combine information from many types of investigations, and we must also (2) continue to restudy old problems in the light of new and sometimes apparently unrelated information. The invitation to write this review caused me to combine information from a current research interest – brittle fracture – with an old interest – relaxation. While reviewing the literature in an effort to get up to date, I discovered many works which I had overlooked in pursuit of a current, perhaps somewhat narrow interest. In this paper, I shall try to put some of these pieces together in order to evaluate our position and outline our understanding of some aspects of the mechanical response of silica glass.

In general, the subjects of strength and viscosity or viscoelasticity are considered quite separately. Fracture is studied at room temperature, is nonlinear and in general occurs at very high stresses resulting from stress concentrations at “cracks”. Flow is studied at low stresses and elevated temperatures where cracks are presumably of little importance. On the other hand, as pointed out by Bartenev,¹ in the ideal situation when the glass surface in both cases is essentially flaw-free, failure and flow presumably occur

by rupture of Si-O-Si bonds and their behaviors are described by:

$$\text{BRITTLE FRACTURE: } \tau = \tau_0 \exp \left[\frac{E - V^* \sigma}{kT} \right] \quad (1)$$

$$\text{FLOW: } \tau = \tau_0 \exp \left[\frac{E}{kT} \right] \text{ where } \tau = \eta/G \quad (2)$$

where τ is the failure time or flow time V^* is the activation volume, σ the stress, η the viscosity, G the shear modulus, and E is the activation energy or the bond energy. In addition to describing our understanding of these properties I will try to illustrate some connections between them.

II. FOUR-COORDINATED NETWORK GLASSES

Before starting the main discussion, it is important to recognize that in SiO_2 (and probably to some extent in other simple 4 coordinated network glass formers such as GeO_2 , BeF_2), many properties are in some way “anomalous”, and in general related to this continuous 3 dimensional network. Some such properties are:

1. Positive temperature coefficient and negative pressure coefficient of elastic constants.²
2. Arrhenius temperature dependence of viscosity.³
3. Very small ΔC_p and $\Delta \alpha$ between glassy and supercooled conditions.
4. Lack of shear flow under pointed indenters.⁴
5. Negative pressure coefficient of viscosity.⁵

Although it is safe to say that none of these effects is really well understood, it is generally felt that the structure of these glasses: the corner-sharing of very stable tetrahedra (4-fold coordinated cations and 2-fold coordinated anions) is in some way responsible. For instance, the strong continuous bonding makes shear flow difficult. The open network which results from the coordinations described makes bond-bending easier than bond stretching or contracting. Also, although detailed models are not available, certainly the small configurational entropy which results from this network plays an important role.⁶ The issue which we would like to pursue here, however, is what is the role of point defects in these anomalies; particularly in the processes of fracture and flow?

III. VISCOSITY AND VISCOELASTICITY

We start with a discussion of flow since it is a bulk behavior, and then discuss fracture where surface perfection is certainly critical. While there has been general agreement that the viscosity of pure fused silica is Arrhenius (ie described by a straight line $\log \eta$ vs. $\frac{1}{T}$ plot, and thus a single activation energy), this has at times been questioned. Fontana and Plummer³ analyzed their data and that of Bruckner⁷ and found $E_{\eta} = 5.30 \pm 0.07$ eV from 1700-2000°C and $E_{\eta} = 5.52 \pm 0.1$ eV from 1235-1335°C. Since these data are barely outside the 90% confidence limits, they concluded that a single activation energy description was adequate from 1235 to 2000°C. Recent work by the present author¹⁰ has also confirmed this up to $T = 2300^{\circ}\text{C}$. Most early workers found that variations in the normally-found impurities had important effects on flow behavior. Hetherington et al⁸ found that anion impurities lower the activation energy

and that cation impurities mainly affect η_0 , the preexponential constant. Leko et al⁹ on the other hand found both E and η_0 were affected by changes in either type of impurity. Figure 1 shows the data of Paek et al¹⁰ for four types of silica containing a variety of both cation and anion impurities at levels of the order of 500-1500 ppm. What is interesting in this data is that the viscosity of all four samples is approximately the same at $T \sim 2500^\circ\text{K}$. Since the viscosities are the same at this temperature regardless of impurity level, it suggests that at this temperature thermally-generated defects outnumber the chemical impurities and thus control the viscosity. As may be seen later in this discussion, concentrations of the order of 10^3 ppm for thermally created defects at this temperature may not be unreasonable.

Before discussing the details of viscous flow, let us briefly consider what is known of the viscoelastic behavior of fused silica. The deformation/time behavior of a normal oxide glass at constant stress, at or above T_g , its glass transition, is shown in Fig. 2. ϵ_i , ϵ_d and ϵ_η are the instantaneous, delayed elastic and viscous responses. As indicated, both elastic responses are recoverable, while the viscous response is not. Phenomenologically, viscous flow and viscoelasticity are often described by means of the spring and dashpot models shown in Fig. 3. In these models the instantaneous elastic response results from elongation of the springs with no dashpot relaxation. Delayed elastic or viscoelastic response occurs as the dashpot is activated by the springs, and only irreversible viscous flow occurs when the springs have reached their equilibrium extensions and is due to constant flow of the combined dashpots. Newtonian viscous flow can be represented by a Maxwell model – a single spring and dashpot in series – and described by the equation $\eta = G\tau$, where τ is the relaxation time of the dashpot and G is

the modulus of the spring. In general for oxide glasses however, this single element is not adequate since it does not account for delayed elastic behavior ie. creep or stress relaxation, nor does it account for the fact that their observed distribution functions are broader than a single exponential. In fact, it has been shown that in the case of B_2O_3 in a narrow temperature range, the relaxation is exponential¹¹ and therefore as expected, no delayed elasticity in shear is observed. As indicated however, this is not generally true and an expression of the following form is used:^{12,13}

$$\varepsilon = \varepsilon_i \exp (t/\tau)^b \quad (3)$$

For oxide glasses and for some polymers the time distribution is relatively narrow $b \sim 0.5$ and the relaxation takes place over about 3 or 4 decades of time.

Many oxide glasses, ie. soda-lime-silica and sodium silicates, can be adequately represented by an equation of the form of eqn. 3 with $b \sim 0.5$ which is *independent of temperature*.¹⁴ This temperature independence is termed thermorheological simplicity (TRS). In addition, most oxide glasses show linear behavior with respect to stress; that is, the relaxation function is independent of the initial stress level. While this latter is found to be the case in silica, there is not general agreement as to its thermorheological simplicity. Mazurin,¹⁵ Mills¹⁶ and Bucaro¹⁷ all find simplicity, though often in a narrow temperature range. On the other hand, not only does Leko^{18,19} find b to vary, he finds other instabilities as well. It is not clear whether these instabilities are intrinsic or not, however. For instance, Nemilov²⁰ has seemed to imply that these behaviors were the result of incomplete stabilization due to incomplete recovery of stoichiometry. The results of Leko might be set aside because of this, but it is interesting that at $\log \eta \sim 10^{13}$

P, Mazurin finds $b \sim 0.5$, in agreement with that found for multicomponent glasses, while at $\log \eta 10^7$ P Bucaro finds $b \sim 0.7$, even though both appear to find TRS in their own experiments. One question that may be asked in an effort to resolve this is – what is the precision of such measurements? Mazurin and Klyuev¹⁵ have plotted reduced data for the four types of silicas they studied (electrically melted, gas-melted, gas-melted stretched and synthetic). Their data are reproduced in Fig. 4, showing only a qualitative indication of the spread of their results i.e., $\pm 5\%$. They believe that most of the observed scatter results from a variation in properties of the glasses themselves rather than errors of measurement. Leko^{18,19} gives 0.95 confidence levels of ± 0.04 in b and $\pm 12\%$ in Gd_d . These are difficult measurements to make because of high temperatures, fairly long times, and problems with devitrification and stoichiometry and stabilization.

All of the data from references 15, 16, 17, 18 and 19 have been normalized in strain and shifted to a common time of $\left(\frac{1}{e}\right) \epsilon_N$. These data are plotted (Fig. 5) as $\log \left[-\log \left(1 - \frac{\epsilon_t}{\epsilon_d} \right) \right]$ vs t to illustrate b (the slope) and the variance, in the data. The correlation coefficient for the least squares line shown, with $b = 0.56$ is 0.974 with a standard error of the estimate of $\sim 10\%$. From this and the estimates of the overall “error” of Mazurin and Leko, there seems little justification for a value of b which changes with temperature, nor one which changes drastically with impurity level. The lack of change of b with temperature might be expected in view of the apparently small changes in configuration with temperature in silica.

This viscoelastic work has an impact on our understanding of viscosity for the following reason. Eisenberg and Teter²¹ have shown, especially in phosphate glasses, that flow occurs by a bond interchange mechanism when the relaxation distribution is rather narrow, eg. $b \sim 0.5-0.7$ as shown by silica. It was argued by Smyth^{22,23} and others however, that such a mechanism is difficult to visualize in a perfect silica network with no defects. Smyth thus developed a model which allows formation of defects, such as, 3-coordinated silicons and/or singly-bonded oxygens, to account for both delayed elasticity and viscous flow (Fig. 6). More recently Brawer²⁴ has carried out molecular dynamics simulations of BeF_2 , a network that is known to be similar to SiO_2 . He found that both 5-fold coordinated Be and 3-fold coordinated F ions are generated. Although it is normally expected that diffusion and/or flow will occur at vacancies, flow in this case is triggered by *over* coordinated sites. In both of these models, the thermally-produced defects act as sites for flow as shown in Figs. 6 and 7. Several other investigations have suggested similar defect models for flow in these networks.^{20,25,26}

It was suggested in section III of this paper that defect concentrations of the order of 10^3 cm^{-3} might explain the convergence of the viscosities of silicas with different impurity types and concentrations at 2500°K. Silin²⁷ et al have estimated the temperature dependence of the numbers of moveable defects (a-type \equiv 3-fold coordinated silicons and b-type \equiv non-bridging oxygen atoms) and stable defects ($N_A \equiv$ oxygen vacancies and $N_B \equiv$ peroxy linkages). According to this model if it is assumed that the total number of moveable defects $n = n_a = n_b$, then

$$n = 2N_A \ell^{-E_a/kT}$$

with $E_A = 1.44$ eV the Si-Si single bond energy, at $T = 2500^\circ\text{K}$, $n \sim 10^{18} \text{ cm}^{-3}$ or ~ 1000 ppm. This is of the order of chemical impurities normally found in silica and thus these defects would be expected to control the flow at this temperature.

Many studies on inorganic glasses as well as various organic liquids and glasses have shown that the activation energies for viscous flow, stabilization and shear and volume delayed elasticity are usually similar. Thus it is to be expected that the mechanisms responsible are similar eg. a bond interchange mechanisms. On the other hand, creep is an elastic response and is of course recoverable. As can be seen from Table I the magnitude of the instantaneous (E_i, G_i, M_∞) and delayed (E_d, G_d, M_0) moduli are similar and thus the magnitudes of the instantaneous and delayed strains are similar. As far as the author is aware, none of the models so far proposed in the literature explains even qualitatively the similarity in these instantaneous and time-dependent strains.

STRENGTH

Despite persisting misconceptions to the contrary, the tensile strength of oxide glasses is generally well-behaved. This is particularly so for high strength fused silica if second-order effects are not considered. To first order the behavior may be summarized in the following way:²⁸

1. Fibers can be drawn so that the surface is flaw free.
2. In the absence of water on the glass surface the measured strength may be considered to be essentially the "theoretical" strength ~ 14 GPa (2×10^6 psi).
3. In the presence of water (liquid or vapor), the measured strength is a function of time under load, with the calculated strength at $t \sim 10^{-13}$ secs corresponding to the

“water-free” or theoretical strength while the strengths at room temperature and a testing time of 1 sec is ~ 5.5 GPa (delayed failure or fatigue).

4. As indicated in (1) above, silica (and other) fibers can be drawn so that most of the surface is flaw-free, although certain regions will have extrinsic “manufacturing” defects.

The details of the fracture of such a perfect surface are not understood, nor is the detailed mechanism of delayed failure. However, insight might be gained into these processes if the affects of the defects described in the previous section were understood. Indeed, attempts have recently been made to study the effects of “intrinsic” defects on strength.

a) IRRADIATION

In the first case, a rather direct attempt was made to influence strength by neutron irradiation.²⁹ Although the preforms rather than the fibers were irradiated, induced defects were not completely annealed and strength reductions were noted (Fig. 8). An interesting aspect of this work is that although the initial strength is decreased, the fatigue, or delayed failure is slowed, so that the ultimate failure times (at zero stress) are the same. For both glasses, irradiation reduces the initial strength, increases the slope ($\frac{\ell n \tau}{\sigma}$) but retains the same value of τ at $\sigma = 0$. Thus according to eqn. 1, U_0 is unchanged but γ (essentially the activation volume) is increased. The effect of radiation would seem to be a change in local structure either by a configuration change or by a change in defects.

b) DRAW PARAMETERS

Other, more technologically important variables which should correlate with defects, are the affects of drawing temperature, velocity and draw force on the strength of the resulting fibers. Early attempts usually measured the affect of these variables on the extrinsic portion of the strength distribution. Schonhorn et al³⁰ showed a clear drop in the high strength, intrinsic mode from $\sigma = 5$ GPa (700 ksi) to $\sigma = 0.7$ GPa (~ 100 ksi) at a draw tension of 50-200 grams or about 20-120 MPa stress. Since no detailed data on the strength distributions are given, a more complete analysis cannot be made. More recent work by Bouten et al³¹ shows a linear drop in strength with increasing draw force as shown in Fig. 9. Although experiments have not been done to separate draw force and draw temperature effects and distributions or standard deviations are not given in this work either, it is stated that "intrinsic strength depends on the drawing force". Indeed since these tests were made in two point bending which results in a gage length ~ 10-50 μm rather than the 0.61 m length measured by Schonhorn et al, it is more likely that they measured intrinsic behavior. Bouten and co-workers suggested that the surface formed at higher tension would perhaps have a less perfect surface though they gave no model for this. However some insight into the possible details of this behavior may be gained from the extensive works of Hanafusa, Hibino and coworkers.³² In particular they have shown that of the three defect centers which they have found to be draw-induced; E' centers, peroxy radicals and nonbridging-oxygen hole centers (NBOHC), only the NBOHC shows a temperature/tension trend similar to that shown by tensile strength (Fig. 10). If this is indeed the case, it might be suggested that the strength is decreased by the presence of NBOHCs; however the exact mechanism is not known. If the

NBOHCs are distributed *randomly* either in the bulk *or* on the fiber surface it is not clear how increasing numbers of random point defects would give rise to a rather continuous decrease in strength. Using the macroscopic Griffith equation or fracture mechanics equivalent

$$\sigma = \frac{\sqrt{E\gamma}}{c} = \frac{K_{IC}}{yc^{1/2}} \quad (5)$$

it can be seen that what is important is the size (c) rather than the number of defects present. It is interesting that recently Weeks and Kinser³³ suggested the possibility of oxygen defect *clusters* in GeO_2 to explain $P_{\text{O}_2} = 1$ behavior.

Some additional insights into stress-generated defects can be obtained from a more recent paper of Hibino and Hanafusa.³⁴ In this work they studied the growth of the intensity of photoluminescence at 650 nm (shown to be proportional to NBOHC) under stress at room temperature. They applied stresses up to 4 GPa and estimated defect concentrations (which were proportional to the applied stress) of less than 10^{14} spins/gram, presumably through the volume of the fiber.

c) CRUSHING

Another quite interesting experiment has been described by Tomozawa et al.³⁵ They studied the generation of paramagnetic centers during crushing of a dry synthetic fused silica (Furukawa synthetic <0.1 ppm OH). Both E' and NBOHC are produced with the combined epr intensity increasing linearly with the surface area of the powders (Fig. 10). Crushing in water or nitrogen resulted in essentially no signal of either type, while crushing in oxygen resulted in a somewhat different signal.

While all of these experiments on draw-induced, stress-induced and crushing-induced centers are intriguing, as indicated, the role of increasing *numbers* of defects is not clear. It would seem that further more quantitative investigations of defect generation and its correlation with stress, time, environment, etc, all of those parameters which affect brittle fracture would provide valuable insight into this phenomenon.

IV. SUMMARY

1. It has been suggested that flow in a silica network most probably occurs by a bond exchange mechanism. Models for this flow seem to require some breakdown of the network, either by impurities or by intrinsic network defects.
2. There is disagreement as to the maintenance of rheological simplicity in silica, i.e. are the relaxation spectra invariant in shape with temperature? The analysis shown here indicates that apparent differences in the literature may not be real.
3. It has been shown that delayed shear elasticity can occur in silica, that the delayed strain, ϵ_d , is of the same order as the instantaneous strain, ϵ_i , and that the activation energy for this process is similar to that for viscous flow.
4. Recent studies of paramagnetic defect generation during fiber drawing, during high level stress application, as well as during crushing at room temperature, show promise of unravelling the mysteries of both flow and fracture.

In this paper, only flow above T_g has been discussed. There are equally important and interesting flow behaviors encountered below T_g . These include such things as the fairly well-documented high pressure compaction,³⁶ flow under pointed (e.g. Vickers)

indenters⁴ and compaction by high energy irradiation.³⁷ Other new and intriguing effects are compaction by sub-bandgap irradiation³⁸ and shear flow induced by particle bombardment.³⁹ A study of this complete field, including the presence or absence of brittle failure, ie. cracking, is necessary to complete our understanding of flow and fracture in disordered oxide systems.

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TABLE I

Glass	E_d	E_i	$R \left(\frac{E_d}{E_c} \right)$	Investigator
Electric Melt	$3.8 \times 10^{11} \text{d-cm}^{-2}$	$8 \times 10^{11} \text{d-cm}^{-2}$	2.1	Mazurin/Klyuev ¹⁵
Gas (stretched) Melt	7	8	1.1	
Gas Melt	7	8	1.1	
Synthetic	4.2	8	1.9	
	G_d	G_i	$R(G_i/G_d)$	Leko et al ^{18,19}
Electric Melt	1.7	3.4	2	
	1.1	3.4	3.1	
Gas Melt	0.4	3.4	7.6	
	2.7	3.4	1.25	
	3.6	3.4	0.94	
	M_0	M_∞	$R \left(\frac{M_\infty}{M_0} \right)$	Bucaro/Dardy ¹⁷
Synthetic	1.17	8.93	7.6	

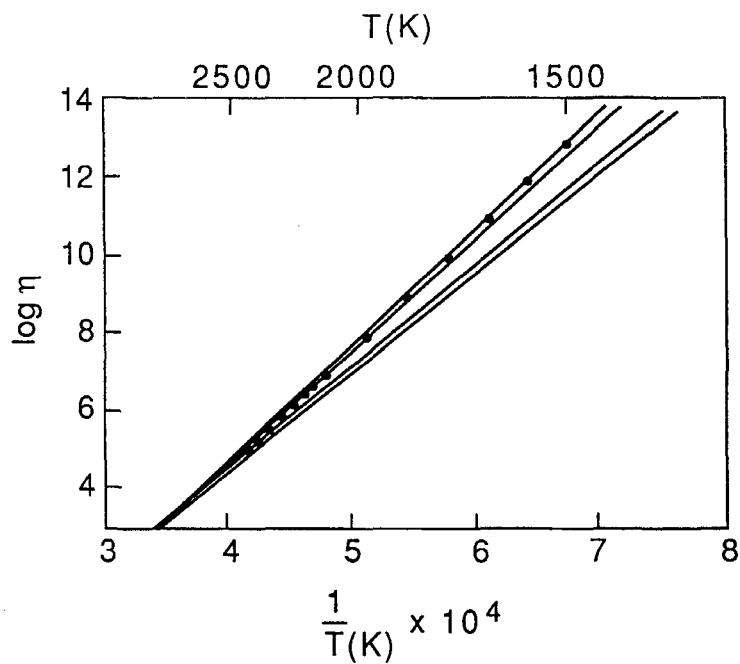


Fig. 1 Viscosity of fused silica samples with differing impurities (100-1500 ppm level).¹⁰

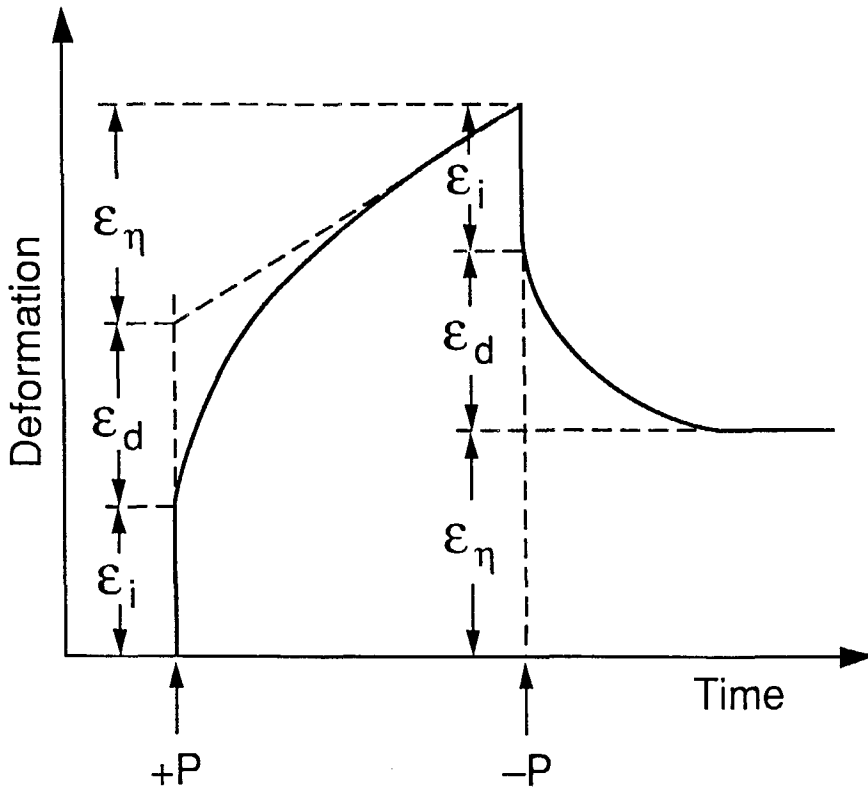


Fig. 2 Deformation (ϵ) of a glass under constant load (P) applied at $+P$ and removed at $-P$. ϵ_i and ϵ_d are the instantaneous and delayed elastic, and ϵ_η the viscous strains.

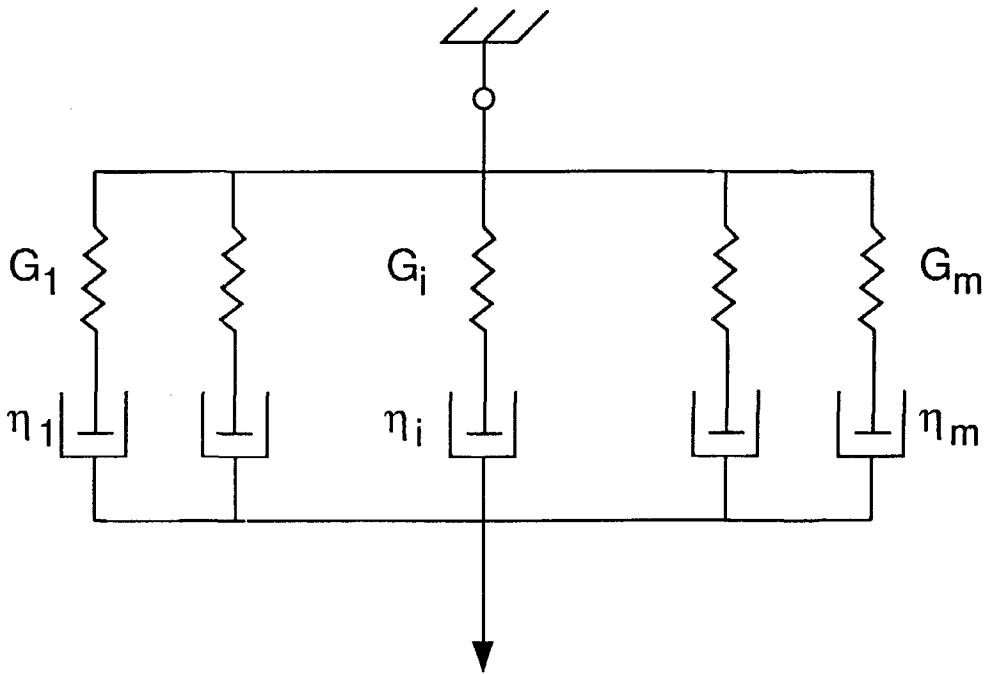


Fig. 3 Parallel Maxwell model; load is applied at the arrow and the deformation as shown in Fig. 2 results. The magnitudes of strain and time are controlled by the stiffness of the springs (G) and the viscosity (η) of the dashpots.

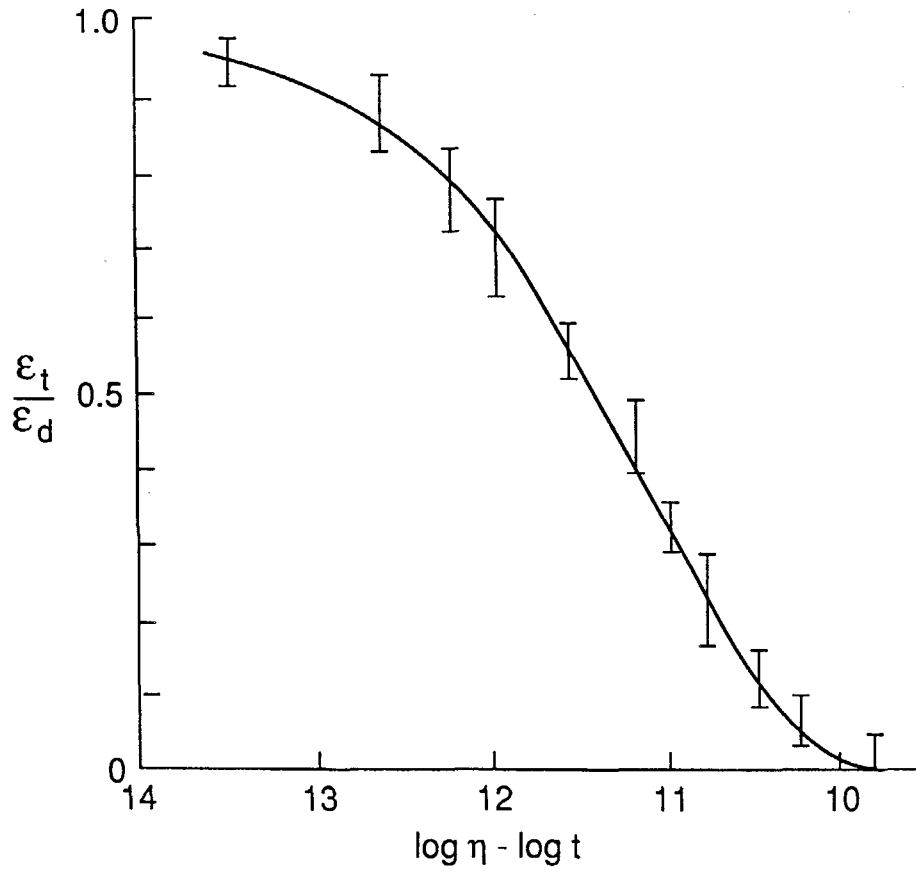


Fig. 4 Composite delayed strain diagram from Mazurin and Klyuev.¹⁵ The error bars are qualitative.

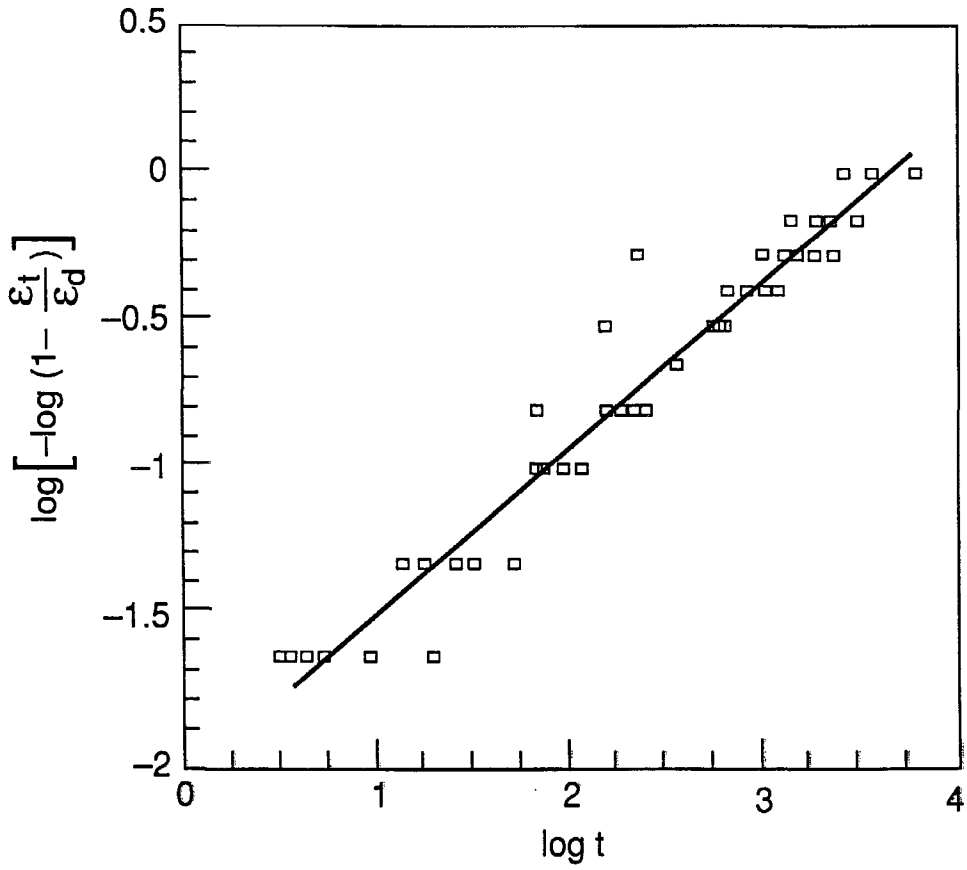


Fig. 5 Normalized relaxation data for fused silica.¹⁵⁻¹⁹ The slope (b) is 0.56, the correlation coefficient $r = 0.974$ and error $\sim 10\%$.

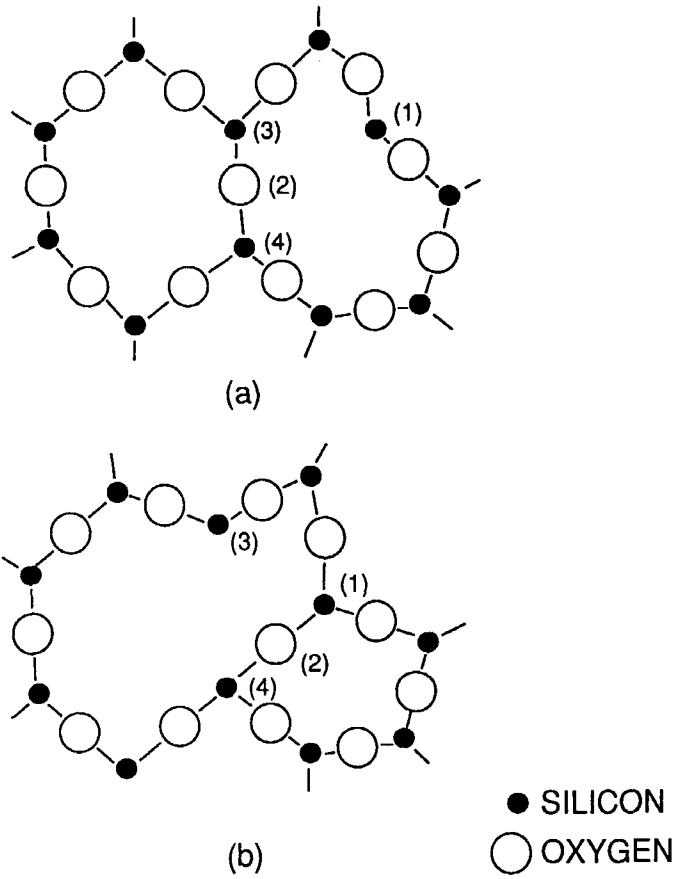


Fig. 6 Model of flow in fused silica (after Smyth²³). The presence of the defect at (1) in (a) (an unsaturated silicon) results in the rearrangement shown in (b).

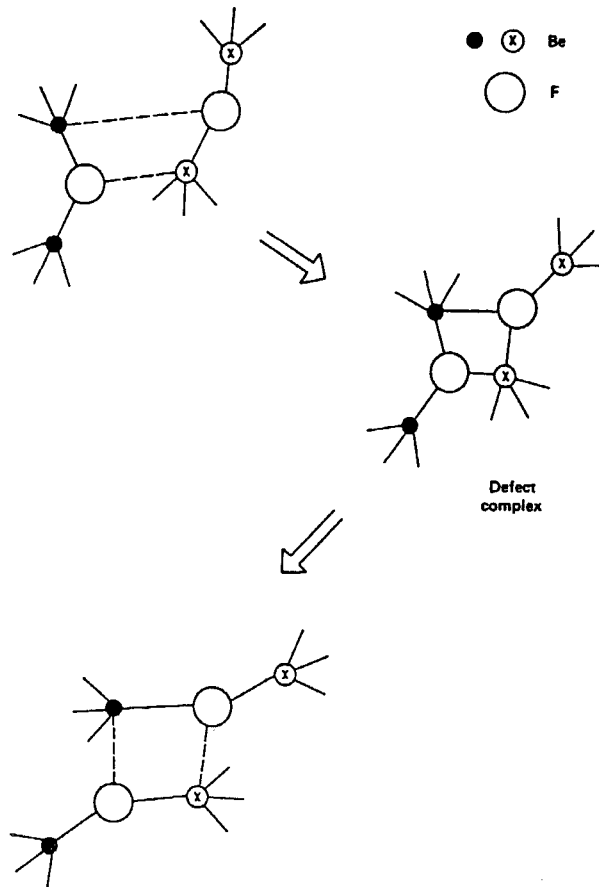


Fig. 7 Model of flow in BeF_2 (after Brawer²⁴). Rearrangements similar to Fig. 6 occur due to the presence of 5 coordinated Be and 3 coordinated F.

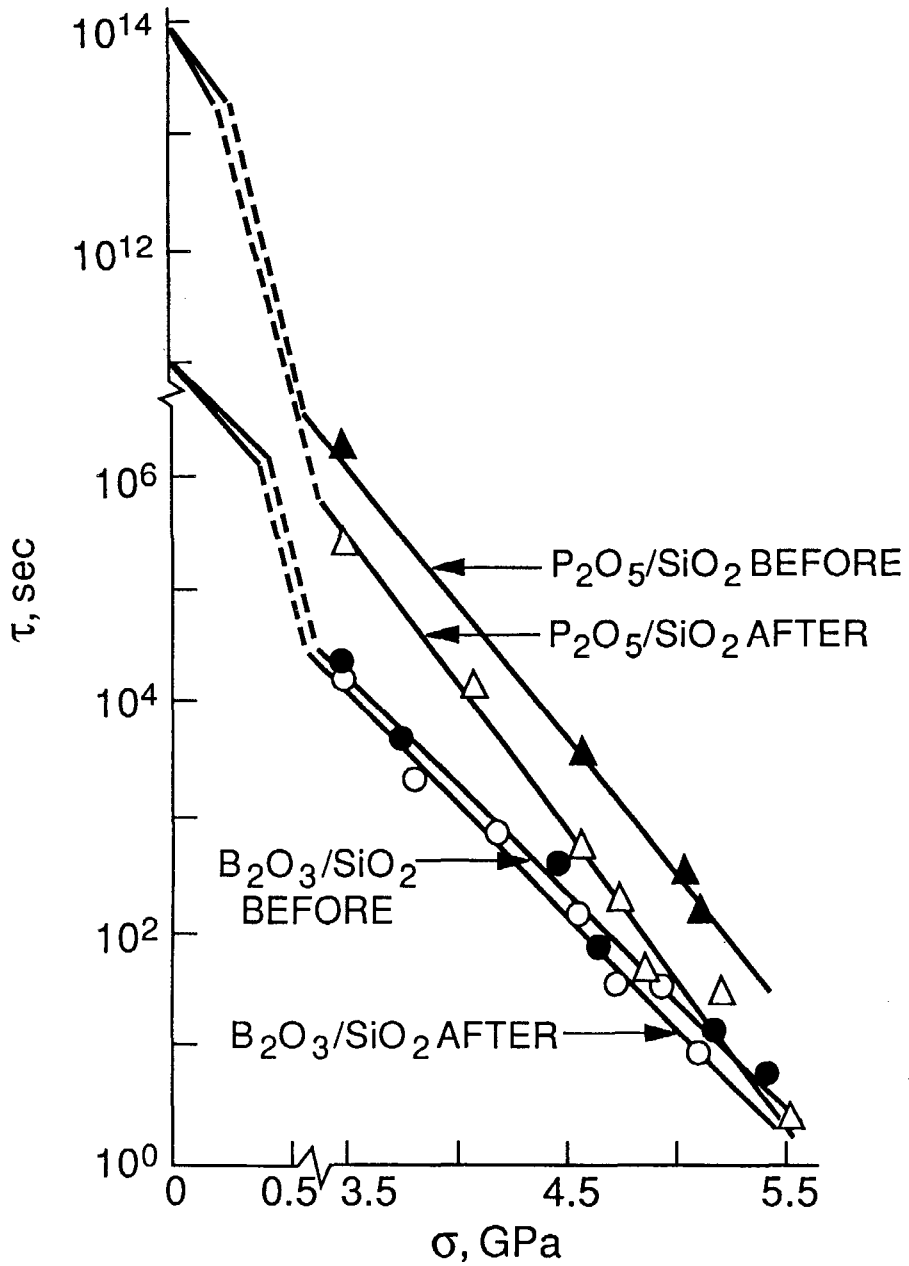


Fig. 8 Delayed failure plot (fatigue) of phospho-silicate and boro-silicate fibers before and after fast neutron irradiation of their preforms.²⁹

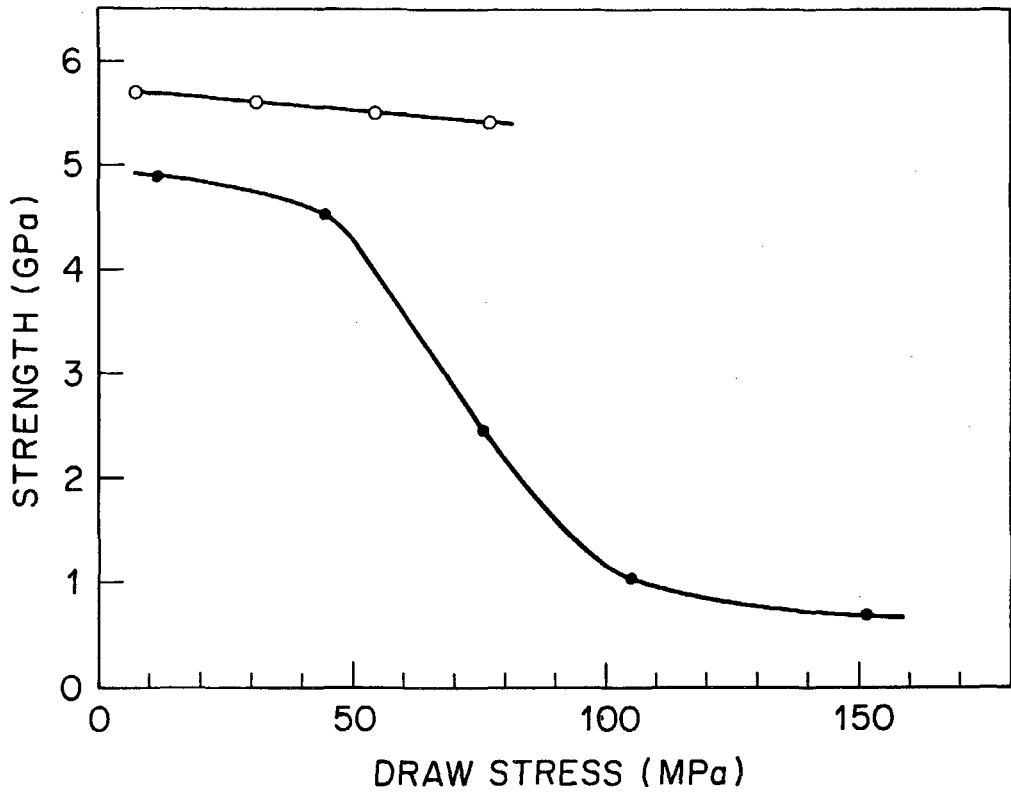


Fig. 9 Influence of draw force on strength of silica fibers. Filled circles Schonhorn et al.,³⁰ open circles Bouten et al.³¹

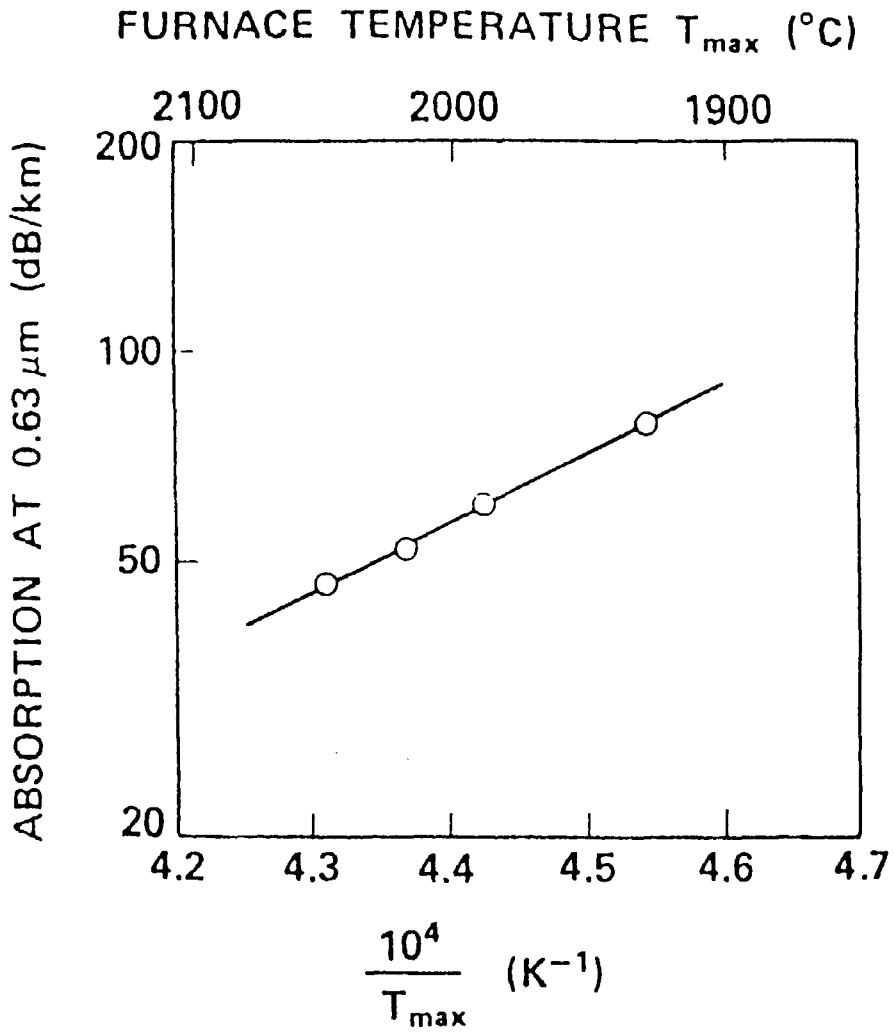


Fig. 10 NBOHC concentration in silica fiber drawn at different temperatures.³²

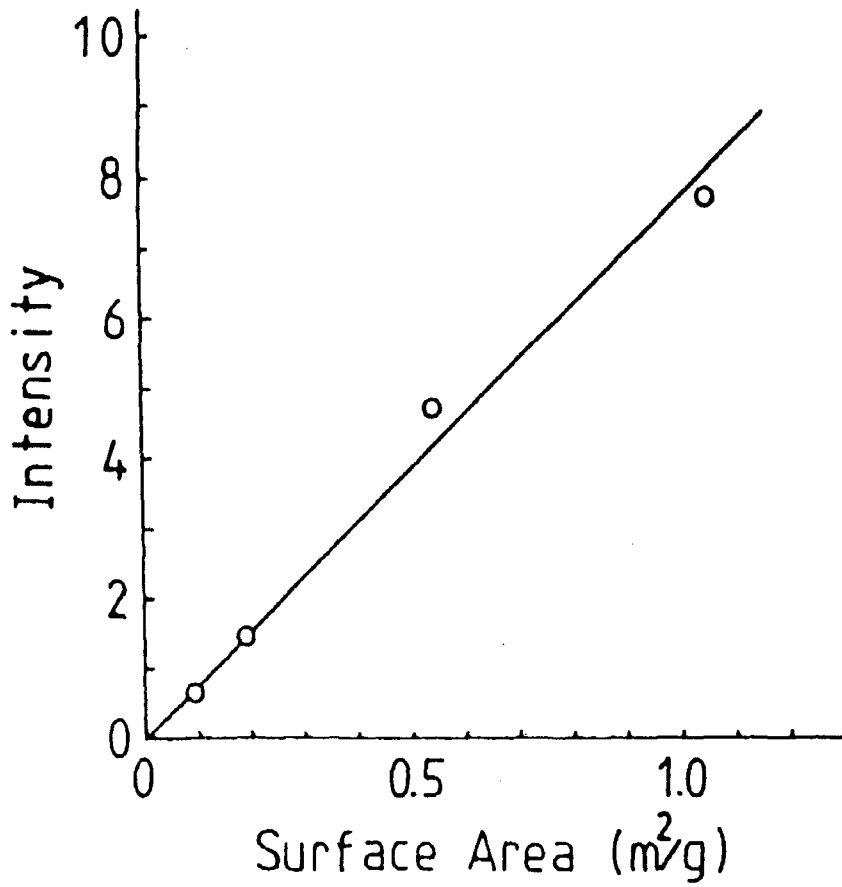


Fig. 11 ESR signal intensity from silica glass crushed in toluene (Kokura et al³⁵).