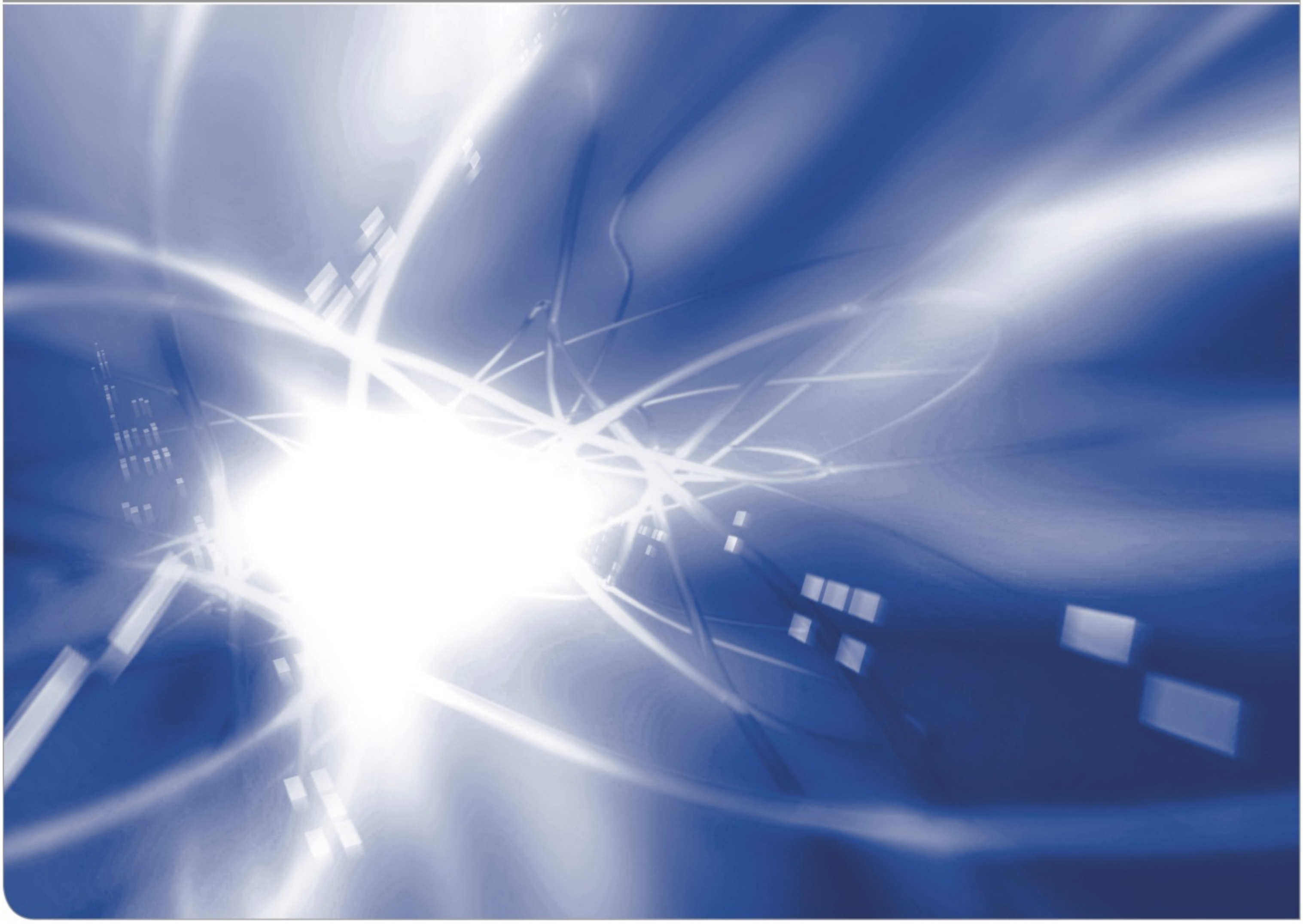
Karlsruhe Institute of Technology

Hydroxyl Damage in Silica:

Full-range description including large damages

T. Fett, G. Schell, C. Bucharsky

KIT SCIENTIFIC WORKING PAPERS **126**



IAM Institute for Applied Materials

Impressum

Karlsruher Institut für Technologie (KIT)
www.kit.edu

2019

ISSN: 2194-1629

Abstract

When water diffuses into silica glass it reacts chemically with the glass forming nanometre sized pores that change the physical properties of the glass. In earlier papers and reports, we discussed the effect of water/silica reaction on the strength via volume swelling, and showed by use of damage mechanics that the water reaction reduces Young’s modulus E and intrinsic strength in thin surface layers. In this paper, the dependency between hydroxyl concentration and damage will be derived for the full damage range by using experimental results from literature. For small water concentrations, we used sound velocity measurements from literature. The suggested relations describe the dependence between the hydroxyl concentration and the Young’s modulus for the damaged glass and allow the strength decrease due to hydroxyl generation to be computed. From an example of application, it can be concluded that damage by hydroxyl generation has little effect on strength even in the case of completely damaged surface region so far the water-affected surface zone is much thinner than the bulk material.

Contents

1 Motivation

Water diffuses into silica glass as a molecule, occasionally reacting with the silica network according to the following equation:

$$\equiv\text{Si-O-Si}\equiv +\text{H}_2\text{O} \leftrightarrow \equiv\text{SiOH}+\text{HOSi}\equiv. \tag{1}$$

The concentration of the <u>hydroxyl</u> water $S = [\equiv\text{SiOH}]$ is usually expressed in terms of the OH-concentration, [OH], whereas the concentration of the <u>molecular</u> water is given by $C = [H_2O]$. This type of diffusion, *i.e.*, reaction-diffusion, was studied extensively by Doremus [1].

When water reacts with silica glass, clear evidence for volume swelling has been reported by Brückner [2,3], Shackelford [4], and Shelby [5], who showed that the density of the silica glass due to reaction (1) decreased, even though the water content of the glass increased. Consequently, the volume also must have increased.

In vitreous solids that have thin surface layers, expansion of the surface layer parallel to the surface of the solid is constrained by the bulk glass. This constraint results in compressive stresses parallel to the surface of the solid; these must be overcome in any strength test, resulting in an increase in the strength of the solid.

On the other hand, the generation of hydroxyl groups destroys the original silica network und must reduce the intrinsic load capability of the network. A question of interest is whether any strength-increasing effect is counteracted by local damage caused by creation hydroxyl groups. This problem was handled in our earlier paper and will be summarized here.

When hydroxyl groups have been formed, silica rings are broken and the mechanical cohesion is weakened. The effect of such "defects" in the glass structure can be treated by using the damage variable D of continuum damage mechanics (Kachanov [6], Lemaitre [7, 8]). This parameter is proportional to the density of micro-defects, $D(S)$. Their regions of influence are symbolized in Fig. 1 by the circles of radius R [9]. The number of defects intersecting the prospective crack plane is then proportional to the number of defects in the volume element.

The damage variable D describes the part of the material cross-section that can no longer transmit forces [7]. The area that can carry load, A_D, is reduced to

$$A_D = A_0(1-D) \tag{2}$$

where A_0 denotes the total geometrical cross section subsuming damaged and undamaged regions.

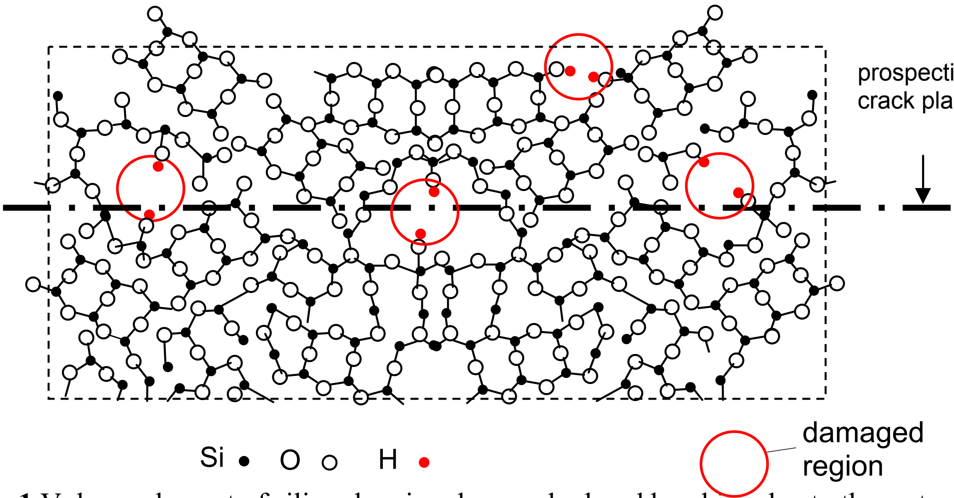


Fig. 1 Volume element of silica showing damage by bond breaking due to the water/silica reaction, third dimension ignored (from [9]).

According to Lemaitre [7], the effective elastic modulus of the damaged glass, E_D, decreases with increasing damage

$$E_D = E_0(1-D) \tag{3}$$

where E_0 is the modulus of the undamaged glass. The damage variable D can be determined from modulus measurements via eq. (3).

Apart from the equi-triaxial loading case with $\sigma_x = \sigma_y = \sigma_z$, the elastic modulus must become a tensor with components depending on the degree of multiaxial loading. This possibility would make the further treatment very difficult [7] and non-transparent. Therefore, we assume in the following considerations that the damage stays isotropic and is of a scalar nature. This is equivalent to the assumption of randomly orientated pore-like defects, in which case, E is isotropic. Therefore, the nano-pores in SiO_2, caused by hydroxyl group generation, behave like normal pores in SiO_2.

2 Experimental evidence for modulus reduction in silica

In the literature, there is experimental evidence for a modulus decrease with increasing hydroxyl content, as reported by Fraser [10] and by LeParc [11]. Both investigators used measurements of longitudinal sound velocity in silica specimens with different water content. Individual least-squares fits were made resulting in the following equations, namely

$$v \cong 5974(1-4.185S) \quad \text{in (m/s)}, \tag{4}$$

For the data set by Fraser [10] and

$$v \cong 5959(1-5.34S) \quad \text{in (m/s)}. \tag{5}$$

for the data set by LeParc et al. [11]

When we normalize the results of the two test series on their individual values for S=0, we get the representation in Fig. 2a. A common straight-line fit of these data yields

$$\frac{v}{v_0} = 1 - B\,S \tag{6}$$

with the parameter B=5.04 [4.23, 5.85] (90% confidence interval in brackets).

Eq. (6) is given in Fig. 2a as a straight line. The longitudinal sound velocity depends on Young's modulus E, Poisson's ratio ν, and density ρ via the following equation:

$$v = \sqrt{\frac{E}{\rho}\frac{1-\nu}{(1+\nu)(1-2\nu)}} \tag{7}$$

For not too large damage (D<0.5) the Poisson's ratio doesn't change more than 10% and can for our purpose assumed as a constant [12].

$$\frac{E_D}{E_0} = \rho/\rho_0 \times (v/v_0)^2 = 1 - \lambda S \tag{8}$$

with λ=10.6 [8.7, 12.5]. This value holds for isotropic damage since the natural OH-content doesn't show any preference for a special direction.

Measurements on porous silica were performed by Adachi and Sakka [13] (see also Yu et al. [14]). The results are shown in Fig. 2b as the circles. The curve shows the best fitting curve according to eq.(10).

A comparable effect on E holds for porosity in ceramics as has been shown by many investigators. Measurements on alumina were compiled very often (Knudsen [15], Wang [16]). Results for hot-pressed silicon nitride (HPSN) with MgO and CeO_2 were reported by Phani and Niyogi in [17] and for reaction sintered Si_3N_4 in [18]. An overview on references is given in [18].

Mostly, the experimental data could be represented in dependence of porosity P by exponential functions of the general type [19]

$$\frac{E_D}{E_0} = \exp[-(b_1 P + b_2 P^2 + ... b_n P^n)] \tag{9}$$

from which for small P follows: $E_D/E_0=1-b_1P$. A description by eq.(9) must of course fail for large porosities since then the requirement of E=0 for a finite critical porosity, at least for P=1 cannot be fulfilled.

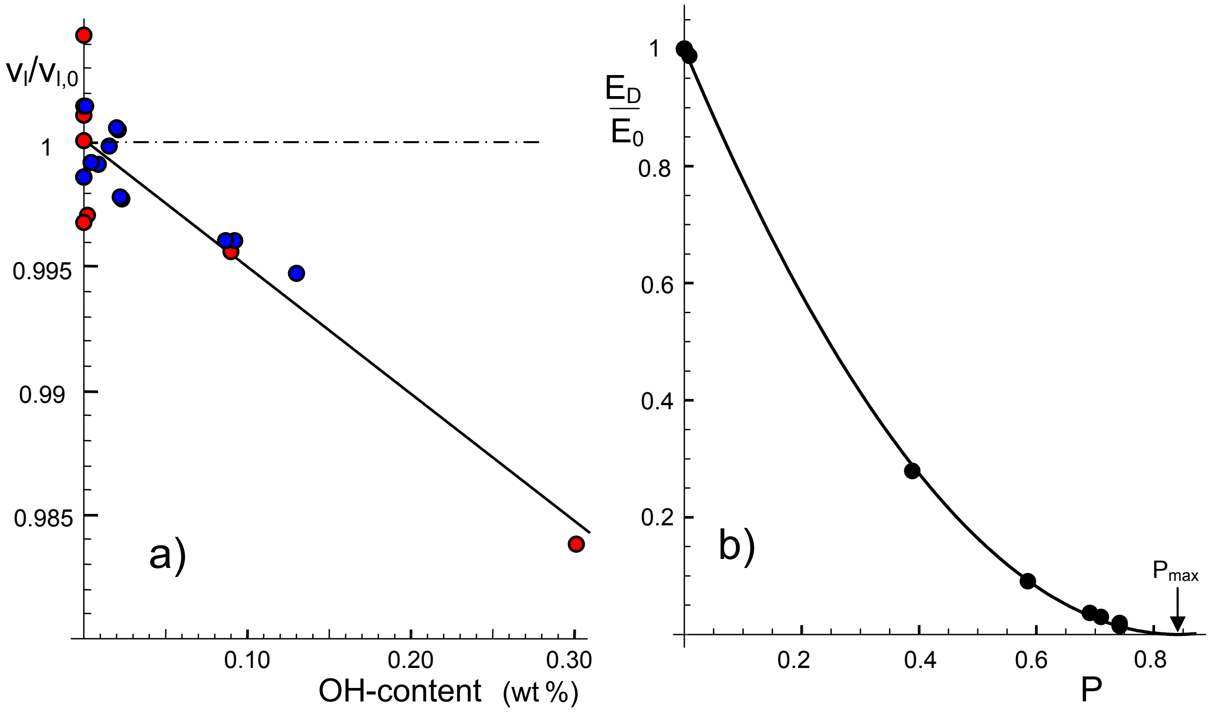


Fig. 2 a) Longitudinal sound velocity in silica with different OH-content (blue circles: results by Fraser [10], red circles: results by LeParc et al. [11]), b) results of porosity on Young's modulus for silica by Adachi and Sakka [13], curve: best fit according to eq.(10).

Analytical computations on the reduction of Young's modulus with porosity were carried out by Wang [19] for spherical pores of equal size. The results showing an upper limit of porosity, are given as sets of tabulated data and were expressed by appropriate fitting relations in [20].

A simpler pore model was proposed by Phany and Niyogi [21] with the result

$$\frac{E_D}{E_0} = (1 - aP)^n \tag{10}$$

By fitting the data of Adachi and Sakka [13], we obtain best representation for the parameter set:

$$n=2,\ a=1.19 \tag{11a}$$

Application of the eq.(10) to the hydroxyl damage gives for n=2 the parameter set

$$n=2,\ a=\lambda/2=5.3 \tag{11b}$$

The maximum hydroxyl concentration that results in disappearing Young's modulus is $S_{\max}=2/\lambda=0.188$. Consequently, the modulus can be described by

$$\frac{E_D}{E_0}=(1-5.3\,S)^2 \tag{12}$$

Figure 3 shows all measurements from Figs. 2a and 2b in a normalized representation. The dashed line illustrates a linear extension of the small-concentration data.

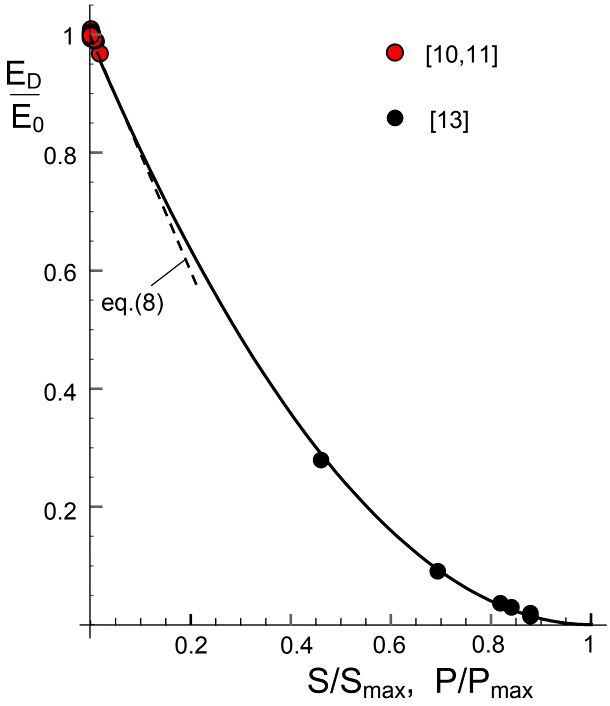


Fig. 3 Young's modulus as a function of hydroxyl concentration and porosity in normalized representation.

3. Strength of a surface-damaged fiber

The hydroxyl-damage in the material also affects the load-bearing capacity of any area element, since it reduces its net cross-section, eq.(2). When $\sigma_{c,0}$ denotes the strength in the absence of hydroxyl damage, and $\sigma_{c,D}$ the strength in the hydroxyl-damaged state, it results

$$\sigma_{c,D}=\sigma_{c,0}(1-D) \tag{13}$$

Let us now consider the strength of silica fibers. First, the water distribution may be replaced by $C=C_0$=const. over the thickness b indicated in the inset of Fig. 4. The total cross section area of the fiber with radius R is

$$A=R^2\pi \tag{14a}$$

that of the inner circle of radius R-b

$$A_{inn}=(R-b)^2\pi \tag{14b}$$

and the ring-shaped area is

$$A_b = R^2\pi - (R-b)^2\pi = (2R-b)\pi b \tag{14c}$$

Failure in the *undamaged fiber* occurs at the surface, when the stress reaches the strength $\sigma_{c,0}$. The force P_0 at failure is then

$$P_0 = \sigma_{c,0} R^2 \pi \tag{15}$$

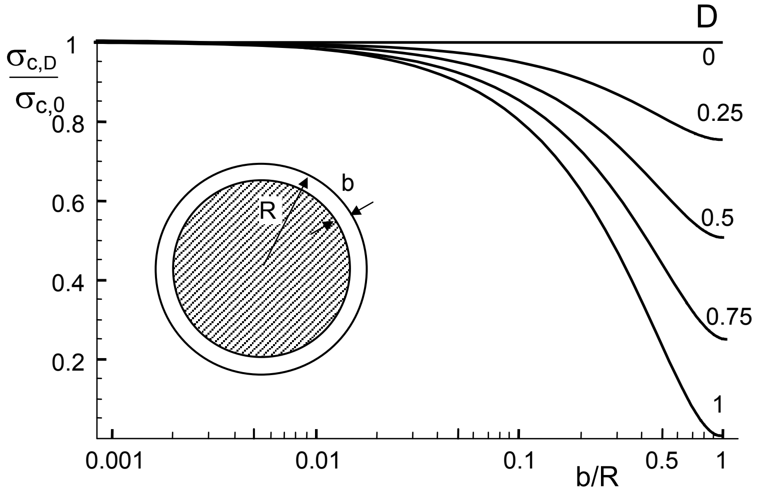


Fig. 4 Strength of a fiber for differently damaged surface regions as a function of layer thickness *b*.

When the surface is damaged by an amount of *D*, the strength in the layer *b* decreases to $\sigma_{c,D}$ according to eq.(13). Since the Young's modulus decreases in the same way, eq.(3), it is clear that the critical strain ε_c remains unaffected

$$\varepsilon_c = \frac{\sigma_{c,D}}{E_D} = \frac{\sigma_{c,0}(1-D)}{E_0(1-D)} = \frac{\sigma_{c,0}}{E_0} \tag{16}$$

The Bernoulli Theorem tells us that plane cross sections must remain plane. It implies that the strain in the damaged and undamaged parts of the fiber must be the same.
This again implies that at failure $\sigma=\sigma_{c,0}$ is in the *inner* area A_{inn} and $\sigma=\sigma_D=\sigma_{c,0}(1-D)$ in the surface layer. The total load P_D of the damaged fiber at failure is the sum of the load in the inner (undamaged) area and the load in the damaged *ring-shaped* zone, i.e.

$$P_D = \sigma_{c,0}(R-b)^2\pi + \sigma_{c,0}(1-D)(2R-b)b\pi \tag{17}$$

The reduction of the fracture load follows from eqs.(15) and (17)

$$\frac{P_D}{P_0} = \frac{(R-b)^2 + (1-D)b(2R-b)}{R^2} = 1 - \frac{2bD}{R} + \frac{b^2 D}{R^2} \tag{18}$$

and is plotted in Fig. 4 for several damage values D as a function of the layer thickness. It becomes clear, that for small ratios of $b/R<0.02$, the strength (computed from the load P_D) is hardly affected as has been outlined in [9].

In the special case of thin layers, $R>>b$, it results approximately

$$\frac{P_D}{P_0} \cong 1 - \frac{2b}{R} D \tag{19}$$

Figuratively speaking, it can be said that even in the absence of any contribution from the stresses in the surface layer, $D=1$, the strength of the entire fiber is hardly affected.

Summary:

We studied the effect of hydroxyl generation accompanied by damaging the initial SiO_2 ring structure. For the mathematical treatment, the damage variable D was used that describes the effective reduction of the load-carrying cross section as suggested by Lemaitre [7]. For small damage, results from literature on sound velocity were transformed into a relation between the Young's modulus for the damaged glass and the hydroxyl concentration. Results for large damage were obtained from literature on the effect of pores on E.

The effect on strength is briefly addressed. We showed in an example of application that the influence of damage is negligible as long as the water layer is about $b/R<0.02$.

References

---

1 Doremus RH. Diffusion of water in silica glass. *J Mater Res.* 1995;10:2379-2389.

2 Brückner, R.. The structure-modifying influence of the hydroxyl content of vitreous silicas. *Glastech Ber*. 1970;43: 8-12.

3 Brückner R.. Metastable equilibrium density of hydroxyl-free synthetic vitreous silica. *J Non-Cryst Solids*. 1971;5:281-5

4 Shackelford JF, Masaryk JS, Fulrath RM. Water content, fictive temperature and density relations for fused silica. *J Am Ceram Soc*. 1970;52:417.

5 Shelby JE. Density of vitreous silica. *J Non-Cryst Solids.* 2004;349:331-336.

6 Kachanov LM. Time of the rupture process under creep conditions. *TVZ Akad Nauk SSR Otd Tech Nauk* 1958;8:

7 Lemaitre J. How to use damage mechanics. *Nuclear Eng Design.* 1984;80:233-245.

8 J. Lemaitre, Evaluation of dissipation and damage in metals, *Proc.I.C.M. 1*, Kyoto Japan 1971;1-16.

9 T. Fett, K. G. Schell, M. J. Hoffmann, S. M. Wiederhorn, Effect of damage by hydroxyl generation on strength of silica fibers. *J Am Ceram Soc*. 101(2018), 2724-2726.

10 Fraser DB. Factors Influencing the Acoustic Properties of Vitreous Silica, *J Appl Phys.* 1968;39:5868-5878.

---

11 Le Parc R, Levelut C, Pelous Martinez JV, Champagnon B. Influence of fictive temperature and composition of silica glass on anomalous elastic behavior *J Phys: Condens. Matter* 2006;18:7507-27.

12 D. Ashkin, R.A. Haber, J.B. Wachtman, Elastic properties of porous silica derived from colloidal gels, J. Am. Ceram. Soc., 73(1990), 3376-81.

13 Adachi, T, Sakka, S., Dependence of the elastic moduli of porous silica gel prepared by the sol-gel method on heat-treatment, J. Mater. Sci. 25(1990), 4732-37.

14 C. Yu, S. Ji, Q. Li, Effects of porosity on seismic velocities, elastic moduli and Poisson's ratios of solid materials and rocks, J. of Rock Mechanics and Geotechnical Engng. 8(2016), 35-49.

15 F.P. Knudsen, Effect of Porosity on Young's Modulus of Alumina, J. Am. Ceram. Soc. 45(1962), 94.

16 Wang, J.C., Young's modulus of porous materials, Part 2, *J Mater Sci*. 1984;19:809-814.

17 Phani, K.H., Niyogi, S.K., Elastic-modulus–porosity relationship for Si_3N_4, J. Mater. Sci. Letters **6**(1987), 511–515.

18 Phani KH, Niyogi KDe. Porosity dependence of fracture mechanical properties of reaction sintered Si_3N_4, *J Mater Sci Letters.* 1988;7:1253–1256.

19 Wang, J.C., Young's modulus of porous materials, Part 1, *J Mater Sci*. 1984;19:801-808.

20 T. Fett, G. Schell, Damage in silica by hydroxyl generation described by Wang's theoretical data, Scientific Working Paper SWP 85, 2018, ISSN: 2194-1629, Karlsruhe, KIT.

21 Phani, K.H. Niyogi, K. De, Young's modulus of porous brittle solids, J. Mater. Sci. **22**(1987), 257–263.

KIT Scientific Working Papers
ISSN 2194-1629