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# Mechanical properties of phosphate glasses

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## Abstract

The strengths of fibers drawn from three metaphosphate glasses [ $\text{NaPO}_3$ ,  $\text{Zn}(\text{PO}_3)_2$  and a Schott laser glass, LG 770, with the approximate molar composition  $20\text{K}_2\text{O}-10\text{MgO}-10\text{Al}_2\text{O}_3-60\text{P}_2\text{O}_5$ ] and a pyrophosphate ( $\text{P}_2\text{O}_7$ ) glass of nominal composition  $40\text{FeO}_3-60\text{P}_2\text{O}_5$  have been measured in 2-point bending at room temperature and at 77 K. While the three metaphosphate glasses have relatively smaller strengths at low temperature ( $\sim 3$  GPa), the iron phosphate glass has a strength at this temperature ( $\sim 6$  GPa), 1/2 that of silica ( $13 \pm 2$  GPa). No correlation was found with either the square root of Young's modulus ( $E$ )<sup>1/2</sup> or fracture toughness ( $K_{IC}$ ), but an understanding of the results was obtained by considering the overall integrity of the individual glass networks. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Strength is usually not the primary physical property of an oxide glass that determines its choice as a desirable material for a given use. In addition, because the practical strength of a glass is often controlled by surface damage, it has been felt that the measurement of intrinsic strength is not pertinent.

Thus, in spite of the very large number of studies which have been made on the tensile strength of oxide glasses over the years, an understanding of their properties is incomplete. Very little information to my knowledge about variations in the mechanical properties, in particular 'intrinsic strength', as a function of glass composition and/or structure is available. By intrinsic I mean the strength of 'pristine' or undamaged (flaw-free) glasses in the absence of delayed frac-

ture or subcritical crack growth (such measurements are normally carried out at 77 K to eliminate the effects of water on strength). The importance of such studies is illustrated by the recent work from Sehgal and Ito [1] on a 'less brittle' glass. This work holds out the possibility of the development of glasses with different and superior mechanical properties. A more complete understanding must be developed, however. It is useful to measure strength and structure in order to more completely understand both.

The mechanical properties of silica fibers [2] have been studied extensively in recent years because of their use as lightguides as have those of E- and S-glasses [3] since they are important commercial fiber glasses. The liquid nitrogen strengths of several alkali silicate glasses were studied in tension over the years by Rindone and co-workers [4], while a variety of simple silicate [5] as well as phosphate [6] glasses have been measured in 3-point bending by Pukh et al. [5]. Very general structural models were used to explain the results of these investigations. Since no careful study of strength as a function of simple glass

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composition has been made, no general conclusions have been possible.

In the present work, a simple 2-point bending technique [7] has been used to make some preliminary measurements on four phosphate glasses. While phosphate glasses are not used as extensively as are silicate glasses, they are of practical interest, especially as laser glasses. In addition they are of fundamental interest because of the variety of structures which can be present in these glasses, and the extensive structural work that has been carried out recently [8–11]. In this paper we present some preliminary strength measurements on simple phosphate glasses to illustrate the importance of carrying out such measurements on a range of simple glass compositions.

## 2. Experimental

The two simple metaphosphate glass samples,  $\text{NaPO}_3$  and  $\text{Zn}(\text{PO}_3)_2$  were prepared by Brow.<sup>1</sup> The sodium glass sample was melted in a platinum crucible (900°C), while the zinc glass sample was melted in a fused silica crucible (1100°C). These latter samples were bubbled with oxygen for 1 h and annealed after cooling at 300°C and 500°C, respectively. The iron phosphate glass sample (40 mol%  $\text{Fe}_2\text{O}_3$ , 60 $\text{P}_2\text{O}_5$ ) was melted by Day<sup>1</sup> in a porcelain crucible in air, and the LG-770 laser glass (approximately 20 $\text{K}_2\text{O}$ , 10 $\text{MgO}$ , 10 $\text{Al}_2\text{O}_3$ , 60 $\text{P}_2\text{O}_5$ , 2 $\text{Nd}_2\text{O}_3$  mol%) was melted in a Pt furnace in air by Schott Glass Technologies.<sup>2</sup> They were re-melted in a Pt crucible at 1000–1200°C in air for approximately 30 min.

The crucible was removed from the furnace and fibers were drawn from the cooling melt using a silica bait rod. The fibers were drawn by hand in approximately 1 m lengths with diameters between 70 and 250  $\mu$ . In practice, sections of  $\sim 5$  cm were tested in 2-point bending [7]. These short sections had variations in diameter of  $\sim 10\%$ . This variation will produce an apparent variation in strength of

this order, or a value of the Weibull modulus ( $m$ ) of the order of 10 to 15. This result was observed in the present investigation. The 2-point bending test measures the tensile strain at failure. This strain is converted to tensile stress using the room temperature Young's moduli according to the equation [7]

$$\sigma = 1.198E d/(D - d), \quad (1)$$

where  $d$  is the fiber diameter and  $D$  is the separation of the 2-point bending plates at failure. Measurements were made at a faceplate velocity of 1000  $\mu\text{m s}^{-1}$  in air at  $\sim 23^\circ\text{C}$ , 50% RH, and while immersed in liquid nitrogen (77 K).

## 3. Results

A Weibull plot of the data is given in Fig. 1. A tabulation of the data is given in Table 1 together with other data from the literature [2–4,6,12,13]. Data for the mean strength at liquid nitrogen are given in column 2. As stated in the experimental section, Weibull  $m$ 's range between 10 and 15. Consequently no error bars are shown in the figures. The strengths from the literature are avail-

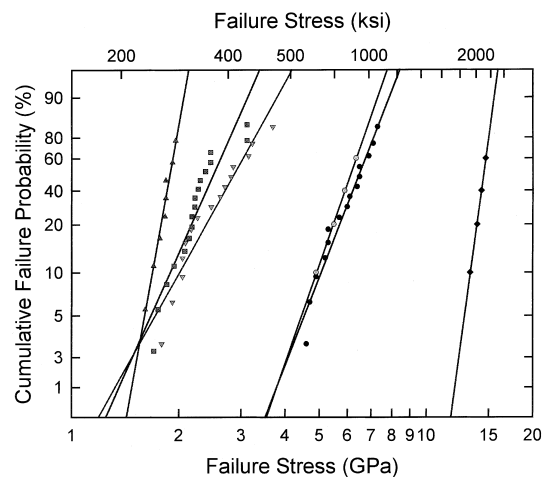


Fig. 1. Weibull probability plot of tensile strength of phosphate glasses and silica. Triangles,  $\text{NaPO}_3$ ; squares, LG-770; inverted triangles,  $\text{Zn}(\text{PO}_3)_2$ ; filled circles, iron phosphate (this investigation); open circles, #8 [6] and diamonds, silica [2]. Lines are drawn as guides for the eye.

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Table 1  
Mechanical characteristics of glasses

Glass	$\sigma_{in}$ (GPa)	$E$ (GPa)	$K_{IC}$ (MPa m <sup>1/2</sup> )	$H_V$ (GPa)	$n^*$
SiO <sub>2</sub>	14	70	0.8	7	20
Na <sub>2</sub> O–4SiO <sub>2</sub>	2.75	63	0.8	3.7	–
E glass	5.8	70	0.9	5.3	30
S-glass	8.4	87	1.27	5.7	40
NaPO <sub>3</sub>	1.8	35.7	0.36	1.8	20 <sup>a</sup>
Zn(PO <sub>3</sub> ) <sub>2</sub>	2.4	42	0.6	2.3	27 <sup>a</sup>
LG-770 20K <sub>2</sub> O 10MgO–10Al <sub>2</sub> O <sub>3</sub> – 60P <sub>2</sub> O <sub>5</sub>	2.3	47.3	0.51	3.2	48 <sup>a</sup> (50 <sup>b</sup> )
40Fe <sub>2</sub> O <sub>3</sub> –60P <sub>2</sub> O <sub>5</sub>	5.9	69.5	0.95 <sup>c</sup>	3.2	34 <sup>a</sup>
(1) 20SrO–10La <sub>2</sub> O <sub>3</sub> –70P <sub>2</sub> O <sub>5</sub>	3.4	58.5	0.7	3.85	–
(2) 25Li <sub>2</sub> O–9La <sub>2</sub> O <sub>3</sub> –66P <sub>2</sub> O <sub>5</sub>	2.7	57.1	0.88	3.8	–
(3) 20K <sub>2</sub> O–10La <sub>2</sub> O <sub>3</sub> –70P <sub>2</sub> O <sub>5</sub>	2.4	47.7	0.82	3.2	–
(4) 15K <sub>2</sub> O–5SrO–10La <sub>2</sub> O <sub>3</sub> –70P <sub>2</sub> O <sub>5</sub>	2.4	48.8	0.57	3.4	–
(5) 25(Li <sub>2</sub> O,K <sub>2</sub> O)–10CaO–5Al <sub>2</sub> O <sub>3</sub> – 70P <sub>2</sub> O <sub>5</sub>	1.8	61.1	0.67	4.2	–
(6) 20(Na <sub>2</sub> O,K <sub>2</sub> O)10Al <sub>2</sub> O <sub>3</sub> –50P <sub>2</sub> O <sub>5</sub>	2.4	55.2	0.5	4.1	–
(7) 35(BaO, SrO, CaO)5La <sub>2</sub> O <sub>3</sub> –50P <sub>2</sub> O <sub>5</sub>	3.3	56.8	0.48	4.0	–
(8) 15ZnO–17.5Al <sub>2</sub> O <sub>3</sub> –67.5P <sub>2</sub> O <sub>5</sub>	5.7	79	0.56	5.4	–

\*These values are measured or estimated <sup>a</sup>using:  $n = \log t / \log \sigma \sim 7 / \log t$  or <sup>b</sup>from  $v$ – $K$  studies [20].

<sup>c</sup>This value was estimated from the linear plot of Ashizuka and Bradt [12] for metaphosphates.

able only at 77 K, and thus only these strengths are tabulated. Approximate room temperature strengths measured in the current investigation may be obtained by dividing that listed at liquid nitrogen by 2. Columns 3, 4 and 5 give data from the literature on modulus, fracture toughness and Vickers hardness, all at room temperature. The data in column 6 are described below.

#### 4. Discussion

At the start, an analysis of the strengths of the silicate glasses is useful. The strength of silica is  $\sim 14$  GPa [2]. The variance ( $v$ ) in strength in Ref. [2] was  $\sim 0.5\%$ , while the variance in diameter was half,  $0.25\%$ . Thus since all of the strength variation can be accounted for by variations in diameter, the strength was assumed not to be due to extrinsic flaws, but due to the intrinsic property of the glass. In addition, since this measurement was made at 77 K, where there is no delayed failure due to the interaction of the glass surface with water, the strength is assumed ‘intrinsic’ [3]. This strength, which is the largest of any oxide glass, may be qualitatively understood by considering that its structure is a three-dimensionally coordinated

network of Si–O–Si bonds. Modification of this network by the addition of alkali ions which produce substantially weaker ionic alkali–O–Si bonds, results in a much weaker structure. The ‘weakest link’ property is evident in the case of the Na<sub>2</sub>O–4SiO<sub>2</sub> glass [4]. It is interesting that while neither the modulus nor the fracture toughness is changed by more than 10% by the introduction of these network modifiers, the intrinsic strength is reduced to  $\sim 20\%$  that of silica. On the other hand, the strength of E-glass [3] is  $\sim 40\%$  and that of S-glass [3]  $\sim 60\%$  of silica. These properties of the two compositions may be rationalized by noticing that S-glass (15% MgO, 15% Al<sub>2</sub>O<sub>3</sub>, 70% SiO<sub>2</sub>) is a ‘stuffed silica’ structure. Thus as alumina is added, an equal amount of magnesium is added for charge compensation. A silica-like 3D structure results. In the case of the E-glass ( $\sim 7\%$  MgO, 19% CaO, 9% B<sub>2</sub>O<sub>3</sub>, 9Al<sub>2</sub>O<sub>3</sub>), no such stuffed silica structure is present, but a structure resembling a modified and weakened silica structure.

More quantitatively, we may try to estimate the strength of a given glass. Such estimates normally combine the force–distance curves for the bonds under consideration with an estimate of the fracture surface energy ( $\gamma_f$ ), i.e., the energy required for producing two new surfaces [12]

$$\sigma = (\gamma_f E / a_o)^{1/2}, \quad (2)$$

where  $\sigma$  is the strength,  $\gamma_f$  the fracture surface energy,  $E$  the Young's modulus and  $a_o$  is the interatomic spacing. Alternatively the Griffith or fracture mechanics expressions may be considered [12]

$$\sigma = (E \gamma_f / c)^{1/2} = K_{IC} / Y c^{1/2}, \quad (3)$$

where  $K_{IC}$  is the fracture toughness,  $Y$  describes the crack shape and  $c$  is the crack length. Thus we see that the strength is expected to be proportional to the fracture toughness ( $K_{IC}$ ) as well as the square root of the modulus ( $E^{1/2}$ ). Such plots for the glasses studied, as well as others in the table are shown in Figs. 2 and 3. Although the arguments to rationalize the relative strengths of silica, sodium silicate, E-glass and S-glass above seem reasonable, neither of the two expected strength correlations suggested seems valid. In particular, the data for silica are displaced to much larger strength. Obviously, more studies of this sort would be useful in understanding the mechanical properties of these simple yet practically important glasses and thus in the design of mechanically superior glasses.

With the above discussion in mind the strength of phosphate glasses may now be considered. In Fig. 1 it can be noticed that the glasses fall into three groups. The mean strength (50% failure probability) of silica is 14 GPa and that of the iron phos-

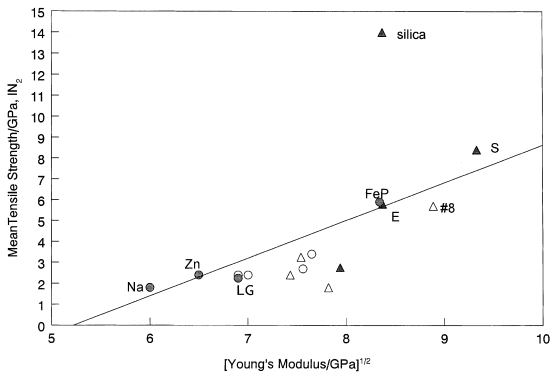


Fig. 2. Mean tensile strength vs. Young's modulus,  $E^{1/2}$ . Filled circles, this investigation; triangles, oxides; open circles, Pukh et al. [6] ultraphosphates; open triangles, Pukh et al. [6], metaphosphates. The line is a least squares fit of the data of the present study ( $R=0.96$ ).

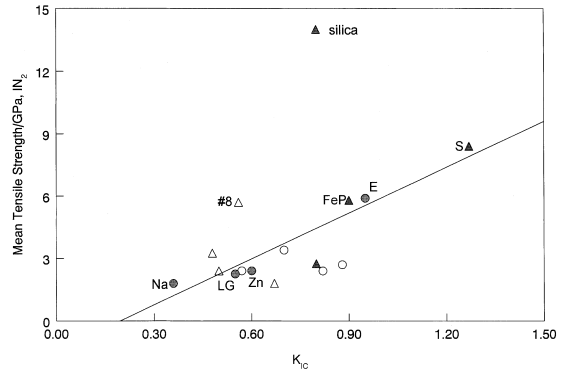


Fig. 3. Mean tensile strength vs. fracture toughness ( $K_{IC}$ ). Filled circles, this investigation; triangles, oxides; open circles, Pukh et al. [6] ultraphosphates; open triangles, Pukh et al. [6], metaphosphates. The line is a least squares fit of the data of the present study ( $R=0.96$ ).

phate and 'Pukh #8' are  $\sim 6$  GPa, while the others fall between  $\sim 1.8$  and 3.4 GPa. The small magnitude of all of the mechanical properties of  $\text{NaPO}_3$  (see Table 1) can be simply understood when one considers that the structure consists of P–O chains, with Na–O–P bonds. Replacing monovalent sodium by divalent zinc results in increases in  $\sigma$ ,  $E$  and  $K_{IC}$  presumably because of the cross-linking by the divalent cations. The properties of the LG-770 laser glass and glasses 2–7 of Pukh et al. [6] also seem explainable on this basis. While divalent or tri-valent cations tend to provide either more cross-linking, or perhaps even the formation of structures stronger and more stable than chains (e.g., rings), it seems that the weakest link' monovalent cations may control the strength and toughness. The incorporation of alkaline earth and aluminum or lanthanum and the elimination of sodium or other monovalent cations generally increases  $\sigma$ ,  $E$  and  $K_{IC}$  (Table 1). As indicated by Pukh et al. [13], however, these increases cannot be explained in detail as one makes these substitutions. Another interesting glass is Pukh #1. While here there are only di- and tri-valent cations, the structure appears to be similar to that found for the E-glass: the relative amounts are not appropriate for the formation of a well-coordinated network and the resulting structure is not as 'strong' as that of Pukh glass #8 nor the iron phosphate glass. The magnitude of the

strengths of these two latter glasses is, to my view, unexpected. They are nearly equal to that of E-glass. While the iron phosphate glass is nominally  $40\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$ , it is known to contain  $\sim 20\text{FeO}$  [14]. Thus these glasses are mixtures of di- and trivalent oxides, but with differing amounts of  $\text{P}_2\text{O}_5$ .

As indicated in Section 1, much structural work has been carried out on phosphate glasses in recent years [8–10]. Hoppe [9,10] has suggested that both  $\text{Zn}(\text{PO}_3)_2$  and  $\text{Al}(\text{PO}_3)_3$  both have silica-like structures, but there has been little research done on glasses containing both di- and tri-valent cations. Brow et al. [11] have studied Na–Al– $\text{P}_2\text{O}_5$  glasses and shown that at larger alumina concentrations both 4- and 5-fold coordinated aluminum ions are formed. However, they found that the increases in the glass transition temperatures at smaller aluminum contents was due to the strengthening of the network by the cross-linking effect of Al– $\text{O}_6$  sites. More structural studies of this sort are in order. On the other hand, work on the structure of the iron phosphate glasses [14] has been interpreted in terms of a structure similar to that of crystalline  $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ . This material contains di- and tri-valent ions in sixfold coordination [15]. The structure contains  $(\text{Fe}_3\text{O}_{12})^{16-}$  clusters with iron ions connecting two phosphate tetrahedra to form a pyrophosphate group. It is not immediately obvious, however, why such a structure should produce a glass of such strength. Again a consideration of Figs. 2 and 3 shows no correlation of strength with either the square root of the modulus ( $E^{1/2}$ ) or fracture toughness ( $K_{\text{IC}}$ ) for the phosphate glasses. While there is a reasonable correlation of the strength of the glasses measured in this investigation and the strength of glass Pukh et al. (#8) with  $E^{1/2}$ , a correlation with  $K_{\text{IC}}$  is absent. In particular, the fracture toughness for the #8 glass appears much too small compared with those of this investigation, as well as with the others which Pukh et al. [6] studied. Perhaps the most striking thing in Figs. 2 and 3 is that while there are substantial changes in both  $E$  and  $K_{\text{IC}}$  for Pukh's glasses as the composition is changed, there is very little change in strength. The exceptions, of course are #8 and the iron phosphate glasses.

As pointed out in Section 1, to my knowledge, very little fundamental work has been carried on

the intrinsic strength of oxide, or for that matter any other, inorganic glasses. Although several molecular dynamic simulations have been carried out the fracture of silica and sodium silicate glasses [16,17], they have provided no insights into the processes which occur in a random system containing bonds of differing strengths. Some theoretical studies [18] have been carried out on synthetic crystals containing randomly placed bonds of differing strengths. Obviously a study of such glasses with a well-designed program of compositional variation is indicated. In addition, complementary theoretical studies are necessary.

The final issue to be considered here is the information contained in column 6 of Table 1. This column gives estimated  $ns$ , the stress corrosion susceptibility or fatigue parameter. This important parameter describes the delayed failure of a glass. It is normally considered to be a power function of stress and is thus the inverse slope of the  $\ln$  stress ( $\sigma$ ) vs.  $\ln$  time plot

$$n = d(\ln t)/d(\ln \sigma). \quad (4)$$

The  $ns$  that appear in column 6 have been calculated by assuming that the strengths in the denominator (room temperature and liquid nitrogen strengths) correspond to times in the numerator of  $10^1$  and  $10^{-8}$  s. That is, I assumed that the 'inert strength' measured at 77 K is that which would be measured in  $t = 10^{-8}$  s. While this number is certainly an approximation [19], it does give some idea about the relative susceptibility of the different glasses to fatigue. Larger  $ns$  correspond to a smaller strength decrease with time under stress. Although we assume that these pristine fibers have no flaws, this term is often described as a 'crack growth' parameter. In fact the  $ns$  shown in this column for the Schott laser glass calculated from the above expression and the measured  $n$  from standard crack velocity measurements are in good agreement [20]. It is surprising that the phosphate glasses measured here show relatively larger  $ns$ . That is, the stress-assisted corrosion appears small even though, with the exception of the iron phosphate glass [21], they are known to be quite reactive with water. The stress corrosion of phosphate glasses appears to be an area for more work.

## 5. Summary

1. Some phosphate glasses (iron pyrophosphate and Zn–Al–metaphosphate) have Young's modulus (70–80 GPa) and tensile strengths ( $\sigma_{IN} \sim 6$  GPa) that are larger than those of monovalent phosphate glasses. These are glasses with no monovalent ions, and with the apparently 'appropriate' amounts of di- and tri-valent oxides.
2. Although there may be a correlation in limited compositional ranges, there appears to be no overall correlation of tensile strength with  $E$  or  $K_{IC}$ .
3. Estimates of the fatigue parameter,  $n$ , have been made and indicate relatively small  $n$ s or smaller rates of fatigue than might be expected in view of their reactivity with water.
4. This work points to a need for further studies of the fundamental mechanical properties of simple glasses.

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