STRUCTURAL RELATIONSHIPS IN VITREOUS INFRARED MATERIALS

Semiannual Progress Report
1 April 1967 Through 30 September 1967

W. C. Levengood
T. S. Vong

November 19c 7

INFRARED AND OPTICAL SENSOR LABORATORY
Willow Run Laboratories
THE INSTITUTE OF SCIENCE AND TECHNOLOGY

Prepared for the Advanced Research Projects Agency, Washington, D. C., ARPA Order No. 269, Program Code No. 5730, and monitored by the Office of Naval Research under Contract Nonr-1224(57)

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Ann Arbor, Michigan

PREFACE

The work reported herein was conducted by the Willow Run Laboratories of The University of Michigan's Institute of Science and Technology for the Advanced Research Projects Agency, Washington, D.C., ARPA Order No. 269, Program Code No. 5730, and monitored by the Office of Naval Research under Contract Nonr-1224(57). Dr. Arthur Diness was the contract monitor.

ABSTRACT

Based on considerations of the important role of microyield in glass-structure studies, a linear relationship was found between the breaking strength of glass and microelasticity. This relationship disclosed that the wide spread observed in breaking strength values within one given glass system is due to localized variations in elasticity. Heretofore, these large deviations in strength have been attributed to unresolved factors such as surface contamination, handling defects, etc. Data presented demonstrate a spatial variability in microelasticity, the form of which determines the strength of glass under nonuniform loading conditions. The practical implications in terms of improving the mechanical properties of infrared glasses are discussed.

Several predictions suggested by a previously defined unified theory of glass structure are examined and they generally substantiate the fact that variations in the basic glass structure are determined by surface flaw parameters and flaw interactions. In particular, this study confirmed that gases bound within vitreous networks can influence mechanical strength.

The surface flaw characteristics and critical stress of flaw formation was determined both in infrared transmitting glasses and in a single crystal. The differences in the flaw parameter values for the crystalline solid and the glasses were as predicted. Induced radiation effects were examined in three glasses representing the basic liquid models, and the changes in flaw characteristics are interpreted in relation to liquid model theory.

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1
INTRODUCTION

The research efforts described herein are for the purpose of improving the characteristics of vitreous materials by devising an empirical theory of glass structure and utilizing it both to indicate how existing glass systems can be improved and to predict new ones. In the current studies emphasis has been placed on gaining a basic understanding of the structural properties of glasses in regard to improving strength, surface corrosion, and thermal shock properties of optical elements such as windows, prisms, and lenses.

At the onset of our present research program, one of the primary objectives was to obtain a more fundamental understanding of bond rupture mechanisms in vitreous systems. A previously outlined unified theory of glass structure was to serve as an important guideline in the realization of this objective [1]. The details of the theoretical model are presented in modified form as an appendix to this report. The ultimate usefulness of this model is manifested in predictions of various types of composition and structural alterations leading to strength improvements, particularly within infrared glass systems.

In the process of refining this empirical theory a completely new and very significant concept concerning the strength of glass has been discovered. In the archival literature the large spread in glass-strength data is generally attributed to unknown surface contaminations such as weathering products, scratches, handling defects. etc. It was recently shown by Levengood, [2] however, that a large spread or standard deviation in strength data also occurs when strength test are conducted on fresh breakage surfaces where contamination and mechanical damage are not influences. By further examining elastic yield processes, the importance of which was pointed out in reference 1, we have shown that the spread in strength data can be completely accounted for by considering the elastic yield at the point of load application. Furthermore, a linear relationship was obtained by plotting the load to cause fracture against empirically determined values of microelasticity. It is shown that this linearity is a fundamental relationship and defines elastic yield variations within microregions of the glass network. Thus, it is clearly demonstrated that there is a spatial variability in the microelasticity, and it is the form of this spatial pattern that determines the ultimate resistance of glass to breaking under nonuniform loading conditions.

This microelasticity relationship was examined in four infrared calcium-aluminate glasses. From the standpoint of the unified glass theory the prediction was made that variations in the slopes of the strength versus microelasticity curves were related to the parameter of flaw

nucleation F_n. This prediction was proved valid and then corroborated by experiments conducted on a different glass system. The calcium aluminate which were melted under vacuum conditions disclosed higher mean breaking-strength value than air-melted samples. These findings confirm the previously suggested importance of considering the presence of gases in the glass network. As far as we are aware, this is the first demonstration that melting conditions can have a pronounced effect on strength levels in glass. Several other predictions based on the unified theory of glass structure were formulated and examined both experimentally and theoretically. These predictions are discussed in section 4.

Another aspect of the current studies is the validation of the unified theory of glass structure, and toward this end we have continued experimental efforts and have discussed our concepts with other workers. Experimentally, we have continued our examination of infrared glasses. The critical stress of flaw formation in two non-oxide glasses was compared with the value obtained in a lithium fluoride (LiF) crystal (also used as an infrared material). Section 6 of the report discusses our contacts with other investigators and their responses to the empirical model. It is our general impression from our visits to other research establishments that glass research is rather confined to specialized areas. Communication between laboratories appears to be limited, and interdisciplinary research is almost nonexistent. As a result of these individual investigations, duplication of effort occurs. Often a scientist working on his own area of interest develops a limited theory for glass structure which does not apply to another glass system or another set of experimental conditions. Because of these factors, the need for a unified and general glass theory became more apparent.

2
COMPARISON OF BREAKING STRENGTH WITH FLAW FORMATION IN NONSILICATE INFRARED GLASSES

Under field usage the failure of most glasses occurs in a state of nonuniform stress loading which may be induced by both mechanical and thermal forces. The infrared glass material used in satellites and missiles offers one exceilent example of environmentally induced nonuniform loading forces. By contrast, most laboratory investigations of the inherent strength of glass are conducted under conditions of uniform loading which tend to average out or deemphasize the influence of local variations in bond strength. Only a few cases have been reported in the literature where the strength of glass has been examined under nonuniform or very localized loading conditions. One of the first of these studies was conducted by Argon, Hori, and Orowan [3] at MIT. This method was later used by Levengood [2] to demonstrate a direct relationship between

the breaking load under localized loading conditions and the formation of linear flaws on fresh breakage surfaces. One of the first questions to be answered in our current research project was whether this same relationship between flaw formation and breaking strength applied to nonsilicate systems. Since considerable information was at hand on the flaw characteristics of four commercial calcium-aluminate infrared glasses, these were utilized in the initial investigation of the breaking load and flaw formation.

2.1. STRENGTH MEASUREMENTS: EXPERIMENTAL PROCEDURE

An Instron tensile-strength tester, located in the Chemical and Metallurgical Engineering Department at The University of Michigan, was utilized in these strength studies. A hardened steel ball 1/8 in. in diameter (used in the Rockwell Hardness Tester) was rigidly mounted on a vertically traveling load assembly. The descent rate of the load assembly was maintained constant at 0.002 in./min. The glass samples were mounted on a load cell with a thousand-pound capacity. The load applied to the test sample was graphically presented on a strip chart recorder. This strip chart recorded the penetration of the sphere into the test sample as a function of the applied load. The significance and utilization of these recordings will be discussed in a later section.

The glass samples used for testing were prepared for mounting on the load cell by forming flat base surfaces on a diamond saw followed by smoothing with fine abrasive. This smooth flat edge prevented erratic mechanical give during a load test. Immediately before testing a fresh breakage surface was formed parallel to the prepared base surface. The steel load sphere was applied directly to these fresh breakage surfaces and the formation of the Hertz cone fracture was taken as the cracking load P_c or breakage value. Thirty or more P_c determinations were conducted on each test specimen. The actual point of loading was separated from the preceding point by at least 2 mm, approximately one order of magnitude greater than the diameter of the contact region. A low-power microscope was focused on the test surface and at the exact moment of formation of the Hertz cone the P_c point was designated on the strip chart. The accuracy of determining the location of P_c on the chart was about ±0.5% of the applied load (estimated from the length of time between the crack formation and notation on the strip chart).

2.2. BREAKING STRENGTH AND FLAW FORMATION IN INFRARED GLASSES

In reference 1 it was shown that for silicate glasses a direct relationship existed between the values of mean breaking strength and the product N_b (measure of total band readjustment in a given network defined by F_1 and F_n) of flaw formation. If this same relationship between N_b and the breaking load exists for other nonsilicate glasses such as those used in the infrared,

this could be an important factor in improving the strength of infrared systems. In the case of the silicate glasses, an increase in the mean value of breaking stress relates to a corresponding increase in N_b. This possibility was examined by comparing the mean breaking load $\overline{P}_c$ in the four calcium-aluminate glasses with the values of N_b. Table I lists these values and the number of strength determinations made on each sample.

The data in table I demonstrate that in both of these calcium-aluminate systems the N_b product is higher for the glasses showing the higher mean strength or $\overline{P}_c$ value. This is what one would expect if the mechanism observed in the silicate glasses is valid for nonsilicate systems. It is not possible to plot all four points on the same curve since these calcium aluminates represent two basically different compositions and therefore cannot be compared on the same basis. It is also interesting to note in table I that the vacuum-melt samples in both cases have a higher strength than the air-melt and this effect of melt is consistent with previously presented defect studies [4]. Thus the data in table I demonstrate that the surface flaw-strength interactions observed in the silicate glasses also take place in nonsilicate infrared systems.

3
DISCOVERY OF A DIRECT RELATIONSHIP BETWEEN MICROYIELD AND INHERENT BREAKING STRENGTH

As previously mentioned under the experimental description in section 2.1, the Instron tensile-strength tester provides a strip chart with a plotted curve of the elastic deformation produced as the ball penetrates the surface of the glass as a function of applied load. This offers a graphic presentation of the manner in which the surface yields elastically in the very localized region under the 1/8-in. steel-sphere load tool. In our previous studies as outlined in reference 1, the microyield of the network was demonstrated to be a structure-sensitive property and related to changes in the type of liquid structure. The microyield was also shown to be inversely related to the parameter of flaw nucleation (F_r). Because of the importance of microyield in relation to our general unified theory of glass structure and its close association with strength, it was decided to examine the details of each loading curve as recorded by the Instron tester.

In figure 1, we have diagrammatically presented the relationship between the steel sphere penetrating the glass surface and the curve plotted on the Instron tester. The deformation versus applied load curve presented at the bottom of figure 1 was obtained from an actual test run. It is noted that this curve is not linear and this is due to the fact that the load device is a steel sphere and consequently the radius of contact area r increases rapidly at the very beginning

TABLE I. COMPARISON OF N_b PRODUCT OF FLAW FORMATION WITH MEAN BREAKING LOAD $\overline{P}_c$ IN INFRARED GLASSES

Calcium-Aluminate Glass	Melting Conditions	N_b	$\overline{P}_c$ (lb)	Number of Strength Tests
SiO_2 doped	Air	0.063	149 ± 54	31
	Vacuum	0.342	203 ± 90	56
BaO doped	Air	0.016	113 ± 64	31
	Vacuum	0.027	226 ± 70	30

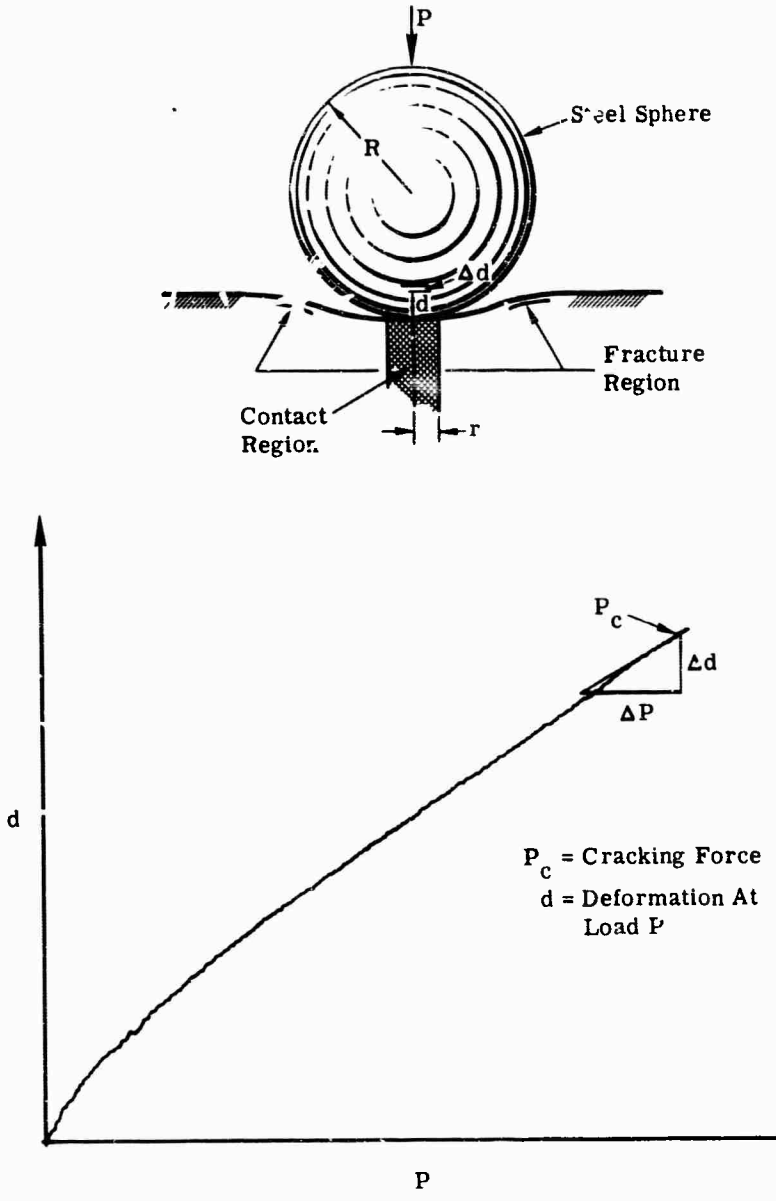


FIGURE 1. DIAGRAMMATIC RELATIONSHIP BETWEEN LOAD P AND LOCALIZE DEFORMATION d. The deformation-load curve is representative of strip-chart test data.

of the load test, then decreases with increasing load. Since we were interested in the actual elastic deformation at the breaking point of each load test, the slope was determined just preceding the P_c value. A fixed increment of load ΔP was taken for these slope measurements. Therefore, with ΔP constant, the slope values $\Delta d/\Delta P$ actually represent variations in the increment of elastic deformation just preceding the point of breakage.

3.1. COMPARISON OF FRACTURE STRENGTH WITH MICROELASTICITY

Since the pressure interval ΔP is held constant for the purpose of slope determination and the slope $\Delta d/\Delta P$ is taken as a measure of the deformation just preceding the crackling load P_c, the elastic behavior in the load region is simply the aggregate response of the individual bonds within the displaced volume. Elasticity is, in general, defined as the force per increment of deformation; therefore, the ratio of the fracture load, P_c, to the incremental deformation just preceding fracture may be considered a measure of the elasticity in the microregion of deformation at the moment of fracture, defined by

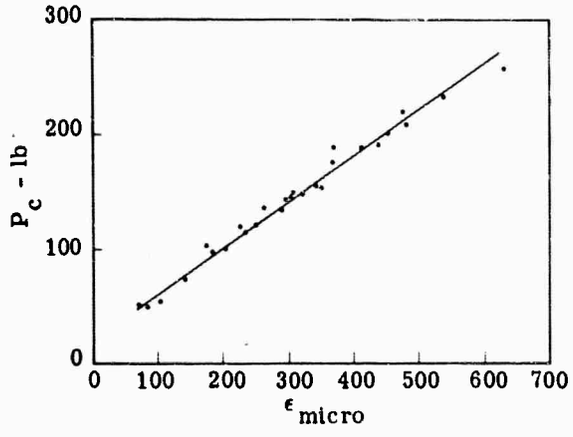
$$\epsilon_{micro} = P_c/(\Delta d/\Delta P) \tag{1}$$

We have used the symbol ϵ_{micro} to designate the microelasticity so there will be no confusion with the use of E which is normally the designation for Young's modulus of elasticity, a measure of yield in the bulk material.

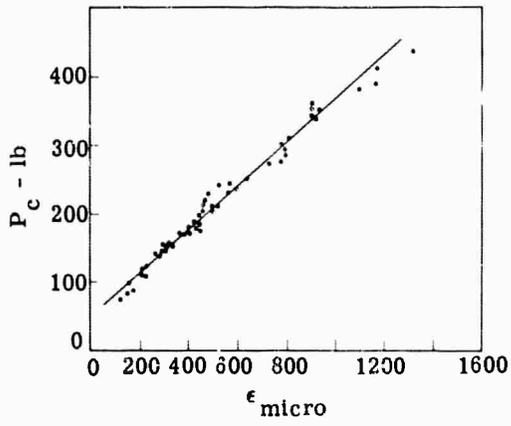
By plotting the values of ϵ_{micro} as a function of the cracking load P_c a linear relationship was found. Each individual breaking load value for the four calcium-aluminate glasses (mean $\overline{P}_c$ values in table I) are plotted in figure 2, parts a through d. The curves were fitted to the data by the method of least squares. The data from these load tests demonstrate that the pronounced scatter in the breakage measurements from fresh cleavage may be explained by localized variations in elastic deformation or microelasticity. This is the first time that a mechanism explaining the pronounced scatter of breakage data has been placed on a quantitative basis. The extreme importance of this method of examining the strength characteristics of various infrared glasses will be discussed in later sections.

3.2. SIGNIFICANCE OF SLOPE VARIATIONS IN P_c VERSUS ϵ_{micro} CURVES

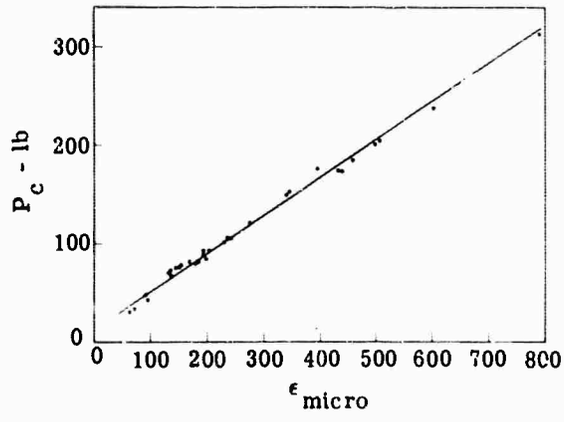
In previous studies [1] relating microyield to the unified theory of glass structure, it was shown that as the flaw nucleation increased the elastic deformation decreased. It was also concluded that the microelasticity at the indenter contact region differs greatly in magnitude and variation from the macroscopic value of Young's modulus of elasticity. At the microscope level



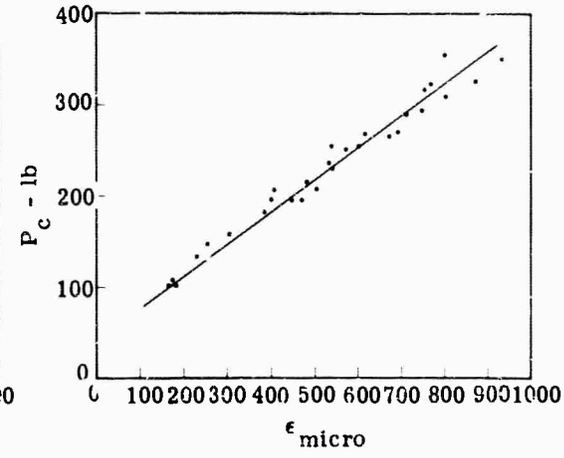
(a) SiO_2 Doped, Air Melt.



(b) SiO_2 Doped, Vacuum Melt.



(c) BaO Doped, Air Melt.



(d) BaO Doped, Vacuum Melt.

FIGURE 2. DEMONSTRATION OF LINEAR RELATIONSHIP BETWEEN BREAKING LOAD P_c AND MICROELASTICITY ϵ_{micro} IN FOUR CALCIUM-ALUMINATE GLASSES (Curves fitted by least squares)

F_n would be expected to vary inversely with the microelasticity (elastic deformation in load region). From equation 1, the relationship to the cracking load is designated by the proportionality

$$P_c \propto \epsilon_{micro} (1/F_n) \tag{2}$$

This proportionality suggests that the manner in which the breaking load varies with ϵ_{micro} is governed by F_n in each particular type of glass. From this proportionality, the incremental change in breaking force with change in microelasticity would be expected to vary with F_n in each type of glass according to

$$dP_c/d\epsilon_{micro} = k(1/F_n) \tag{3}$$

where k is a constant of proportionality. The general relationship between these parameters is expressed by

$$P_c = (k/F_n)\epsilon_{micro} + k' \tag{4}$$

where k' is a constant and F_n is the experimentally determined value of the flaw distribution in each given glass system. The validity of equation 4 may be tested by examining the F_n parameter as a function of slope values taken from experimental data. Thus equation 4 predicts that the change in P_c with local variation in ϵ_{micro} is related to the overall flaw distribution on the fresh cleavage surfaces.

To examine this hypothesis, the slope values were taken from the experimental data in figure 2 and arranged in table II along with the $1/F_n$ values for each of the two calcium-aluminate systems (slope values determined by method of least squares). These data demonstrate that the reciprocal flaw number values increase (F_n decrease) with increasing slope of the experimental breaking strength curves in each of the two systems. These data were not plotted since, as previously pointed out, the calcium aluminates represent two different composition systems. The data presented in table II simply indicate that the slope variations in the P_c vs. ϵ_{micro} curves are indeed, as predicted by equation 4, related to the flaw nucleation on the test surfaces.

4
PREDICTIONS BASED ON THE UNIFIED THEORY OF GLASS STRUCTURE

The results of several predictions based on the unified theory of glass structure (see appendix) are discussed in this section. In some cases, as will be pointed out, these results were suggested during a course of discussions with other investigators. In general, the fact that

TABLE II. VARIATION IN THE SLOPE OF THE EXPERIMENTAL BREAKAGE CURVES (P_c vs. ϵ_{micro}) WITH RECIPROCAL OF FLAW NUMBER ($1/F_n$)

Calcium-Aluminate Glass	Slope ($dP_c/d\epsilon_{micro}$)	($1/F_n$)
SiO_2 doped, vacuum	0.289	0.12
SiO_2 doped, air	0.370	0.89
BaO doped, vacuum	0.330	0.20
BaO doped, air	0.402	0.44

surface flaw parameters and flaw interactions indicate variations in the basic structure of glass and that implications drawn from the basic model may be projected into nonsilicate infrared systems are substantiated by the results of these predictions.

4.1. RELATION BETWEEN STRENGTH AND MICROELASTICITY

The impetus for investigating a possible relationship between the fracture strength and the microelasticity at the point of fracture came about as a result of a previous consideration of microyield properties related to the unified theory of glass structure. Reference 1 pointed out that the empirical calculations of J. C. Phillips at Rutgers University did not disclose a relationship between the macroscopically measured values of Young's modulus E and the flaw parameter F_n even though such a relationship had been anticipated. Consideration of this dilemma brought out the fact that microyield as induced by the application of localized forces is considerably different in magnitude from the macroscopic value of Young's modulus. By examining experimental data, it was indeed shown that when considered in microregions the elasticity was inversely related to F_n.

Based on these considerations and the deformation load curve for each data point on a given test specimen provided by the Instron tester, it was decided to examine in detail the deformation just preceding the fracture load P_c. As shown in the preceding section, what we feel is a very important linear relationship was established when comparing the P_c values with the value of microelasticity ϵ_{micro} determined from the plotted curve. Such a linear relationship now allows us to examine variations in fracture strength from the standpoint of fundamental causations.

4.2. FLAW NUCLEATION INVOLVEMENT WITH THE P_c VERSUS ϵ_{micro} RELATIONSHIP

Equation 4 provides the analytic expression for the data presented in figure 2. This relationship suggests that the slopes of these curves are related to the reciprocal of F_n. As F_n increases, the network becomes more rigid (or more brittle in the common vernacular) and the slope of the empirical curve decreases. Because of the significance of the predicted involvement of F_n (see table II) in determining the slopes of the linear curves, the problem was examined in a different manner.

The fresh breakage surface and the commercially polished surface on ordinary plate glass provide two radically different environments in terms of F_n. On the fresh breakage surface, only the linear flaws are present whereas on the commercially polished surface myriads of microscopic cracks are located below the polished layer. These cracks are covered over by a

polished layer and are not visible; however, they are readily seen with ordinary etching processes [5]. One should expect that the presence of these microscopic cracks in the polished layer would alter the microelasticity values.

The indenter strength measurements were conducted on a fresh fracture surface and on the polished surface of 1/4-in.-thick plate glass. The same sample was used to obtain both sets of data. These data are plotted according to the equation 4 relationship in figure 3 and, as predicted, the values for the polished surface lie on a curve of lesser slope than the data for the fresh fracture surface. The mean cracking-load values $\overline{P}_c$ and the slopes of these curves obtained by method of least squares are presented in table III along with the flaw nucleation F_n values. Because of the large number of flaws and cracks on the polished surface, the F_n figure represents an order of magnitude. The fact that the polished surface discloses a much lower mean fracture strength than the fresh fracture surface is of course as expected. The pertinent factor is the difference in slopes which suggest different flaw nucleation interactions on the two types of surfaces. The lower slope value on the polished surface demonstrates that the macroscopic cracks in the polished surface layer influence the microelasticity characteristics. The results in figure 3 definitely substantiate the hypothesis that flaw nucleation is intimately involved in the fracture process.

4.3. INVOLVEMENT OF DISSOLVED GASES WITH STRENGTH CHARACTERISTICS

Although published data on the subject of dissolved gases affecting the strength of glass is at the present time fragmentary at best, it was previously predicted [1] that dissolved gases in the network of glass would alter the mechanical strength of the system. Furthermore, in an earlier investigation concerning stress-induced surface flaws in the four calcium-aluminate systems [4] it was suggested that the breaking strength would be higher in the vacuum-melted glasses after removel of the OH ions which act as centers of w[illegible]ss in the structure. The data in table I corroborate this prediction; namely, the mean $\overline{P}_c$ values are, indeed, higher in both the vacuum melted glasses which contain fewer OH groupings. Thus we have experimentally confirmed the influence of dissolved gases on the basic strength characteristics. The OH ions actually form chemical associations in the network, and, therefore, their removal results in bond readjustments. By adding interstitial gases which are not chemically bound, one may increase the strength of the system when dissolved water is present.

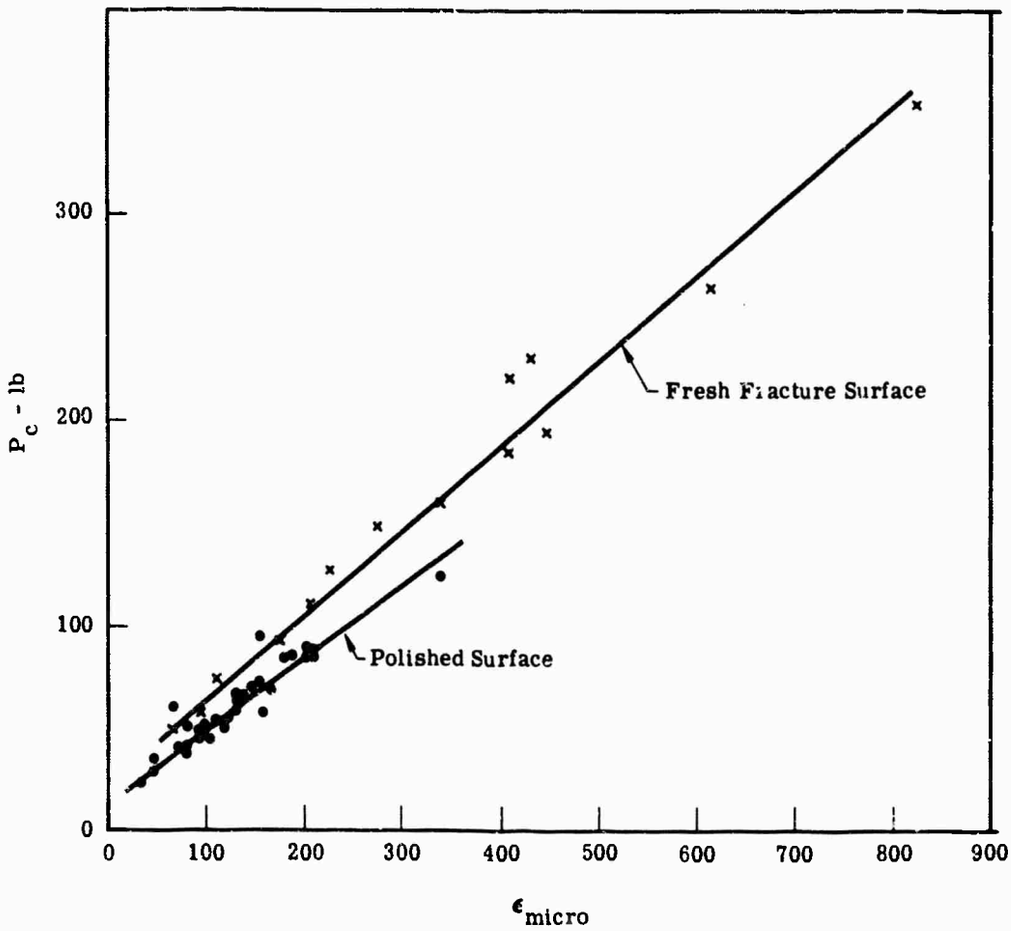


FIGURE 3. SURFACE CONDITIONS INFLUENCING THE BREAKING LOAD-MICROELASTICITY RELATIONSHIP IN A SAMPLE OF PLATE GLASS (Curves fitted by least squares)

TABLE III. FRACTURE STRENGTH VARIATIONS IN TWO DIFFERENT SURFACES ON PLATE GLASS

Type of Surface	$\overline{P}_c$ (mean ± standard deviation)	Slope ($dP_c/d\epsilon_{micro}$)	F_n (flaws/mm)
Freshly fractured	162 ± 81	0.398	2.61
Polished	63 ± 22	0.336	~10

4.4. RELATIONSHIP BETWEEN MEAN BREAKING STRENGTH $\overline{P}_c$ AND THE RATE OF SLOW FRACTURE IN GLASS

Since the point could be argued that the indentation strength as determined by the 1/8-in. hardened steel ball is a special type of fracture, the relationship with microelasticity may not be representative of the situation exemplified in the case of a slow moving fracture. The technique of measuring the rate of slow fracture propagation in glass has been previously presented in the literature [6] and the experimental details will not be reiterated here. The rate of slow fracture was determined in the silicate glasses used to represent the three liquid models in our theory, and fused silica was included in this study. These values of slow fracture rates represent the lateral movement of an internal crack in glass produced under controlled conditions. One would predict, therefore, that the rate of bond breakage at the crack tip would be directly related to the microelasticity or for that matter the breaking load as determined by the hardened spherical indenter. The $\overline{P}_c$ values for these four glasses were previously determined [2] and therefore can be utilized in this prediction. The values of the mean breaking load $\overline{P}_c$ are plotted in figure 4 as a function of the fracture rate. The obvious correlation between these entirely different methods of examining fracture processes demonstrates that the currently used technique of applying the hardened sphere to the fresh breakage surface does indeed provide a fundamental measure of bond breakage.

4.5. RELATION BETWEEN FLAW NUCLEATION F_n AND LIQUIDUS TEMPERATURE

During a visit with Given Cleek, at the National Bureau of standards, the previously recorded relationship [1] between flaw formation in a barium-silicate system and the liquidus temperature was discussed in detail. In this discussion, Mr. Cleek made the suggestion that if F_n is a measure of flaw nucleation in the glass structure then this parameter could be related to liquidus temperature which is also a measure of nucleation centers in the glass network. The three soda-lime-silica systems representing our basic liquid models are of simple composition and Mr. Cleek suggested that we might locate the liquidus temperatures for these three glasses in published phase diagrams. A search of the literature did result in our locating the liquidus temperature values for these three systems. These values as obtained from phase diagrams [7] are plotted as a function of F_n in figure 5. The agreement here is quite amazing; the relationship in figure 5 demonstrates that the F_n parameter should be considered in terms of the crystallization potential in a given glass network.

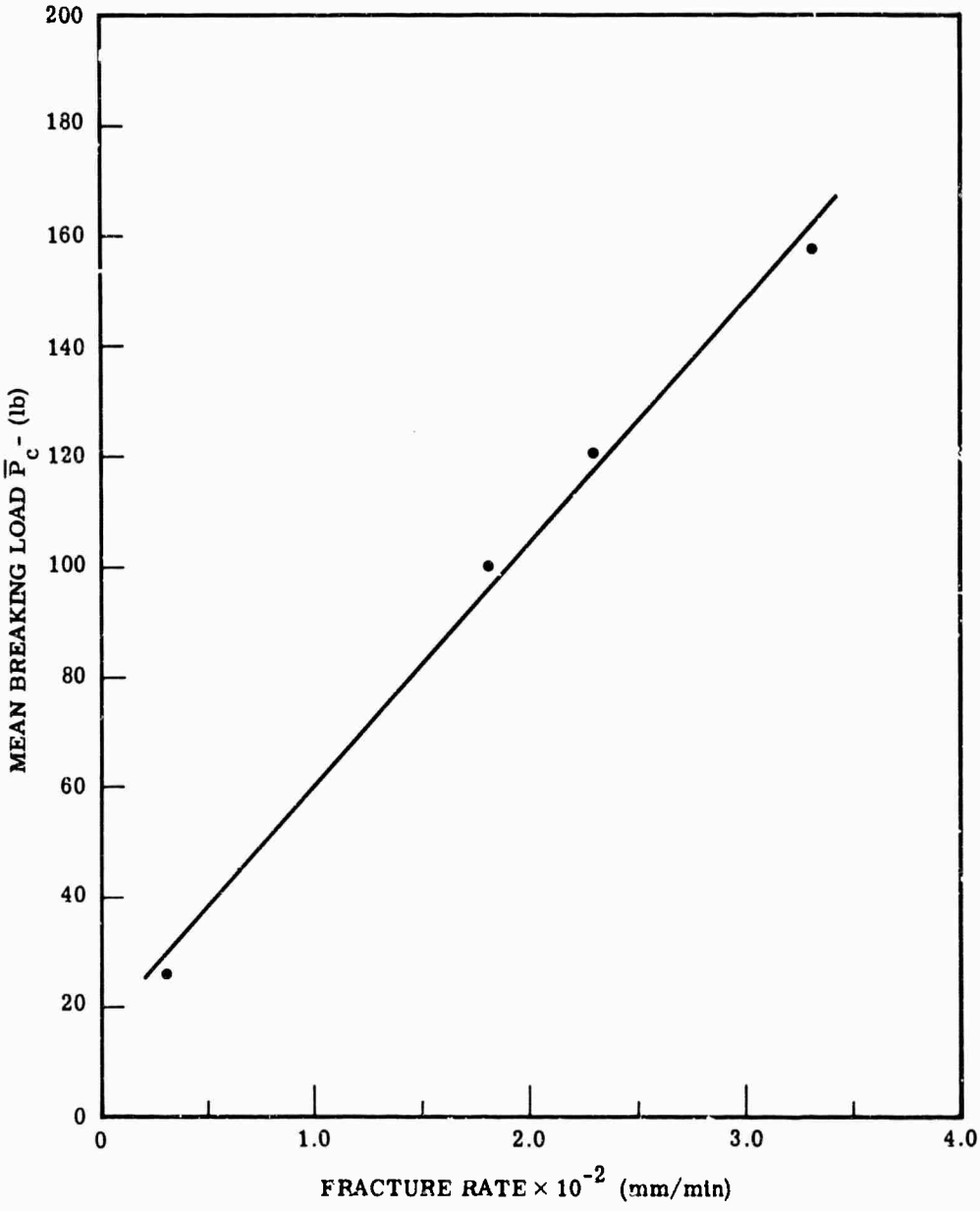


FIGURE 4. RELATIONSHIP BETWEEN THE MEAN BREAKING LOAD AND THE RATE OF SLOW FRACTURE IN FOUR SILICATE GLASSES

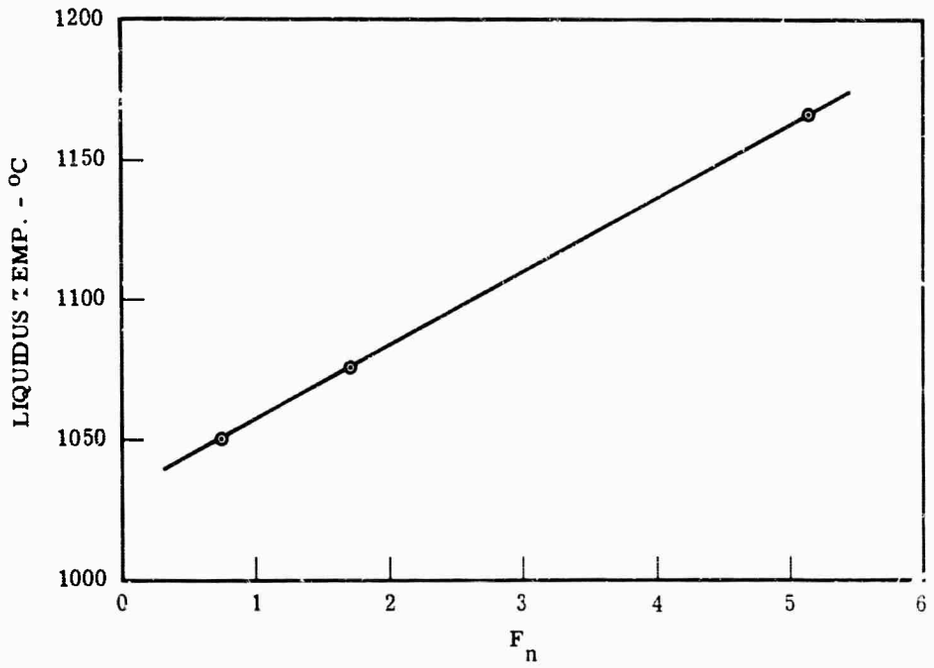


FIGURE 5. CRYSTALLIZATION TEMPERATURE AS RELATED TO THE FLAW NUCLEATING PARAMETER IN THE THREE GLASSES REPRESENTING THE BASIC LIQUID MODELS.

5
APPLICATIONS OF THE THEORETICAL GLASS MODEL

The unified theory of glass structure was examined in terms of extending its usefulness into other types of glass systems. Experiments related to this aspect of the study are discussed in this section. Comparisons of the effects of radiation damage in glasses representing the three liquid models are also included.

5.1. CRITICAL STRESS DETERMINATIONS IN NON-OXIDE GLASSES AND IN AN INFRARED TRANSMITTING CRYSTAL

Based on previous applications of our unified theory of glass structure to various types of silicate systems as well as to crystalline structures, one would predict that the curve of flaw length vs. $P^{1/2}$ would display quite different slope and intercept (b) values for the non-oxide infrared glasses than for an infrared transmitting crystal. The differences in the flaw formation in response to the dynamic indenter forces are demonstrated for three infrared materials in figure 6; the arsenic trisulfide (As_2S_3) is replotted for the purpose of comparison. As previously pointed out, the As_2S_3 glass has a positive b value whereas the germinate glass (Ge_2S_3), although quite similar in physical appearance with As_2S_3 displays a negative b value. From the curves in figure 6 and our liquid model, one would predict that the Ge_2S_3 glass represents a more ordered system and lies in the Frenkel region, while, as previously stated, the As_2S_3 glass is more of a Stewart-type liquid. The critical stress and b values for these three systems are listed in table IV and the LiF crystal, as would be expected in a crystalline system, has a much more pronounced negative b value than even the Ge_2S_3. Sapphire and ruby crystals, for example, also disclose very pronounced negative b values as determined by the indenter technique [8]. The results in figure 6 and table IV demonstrate very clearly that even in the non-oxide systems the indenter technique differentiates positively between a well-ordered crystal system and the vitreous infrared glasses. The pronounced differences in the curves for the glasses and the crystal suggest that by knowing the flaw parameter values the state of crystallinity and orderness within an infrared material may be more clearly defined.

5.2. CRITICAL STRESS DETERMINATIONS IN SYSTEMS REPRESENTING THE BASIC LIQUID MODELS

We have not previously determined the critical stress of flaw formation in the three basic soda-lime-silica systems representing our liquid models. Realizing the importance of these three systems in discussions concerning our theoretical model, the curves for flaw length vs. $P^{1/2}$ were determined and the results are summarized in figure 7. The values of the critical

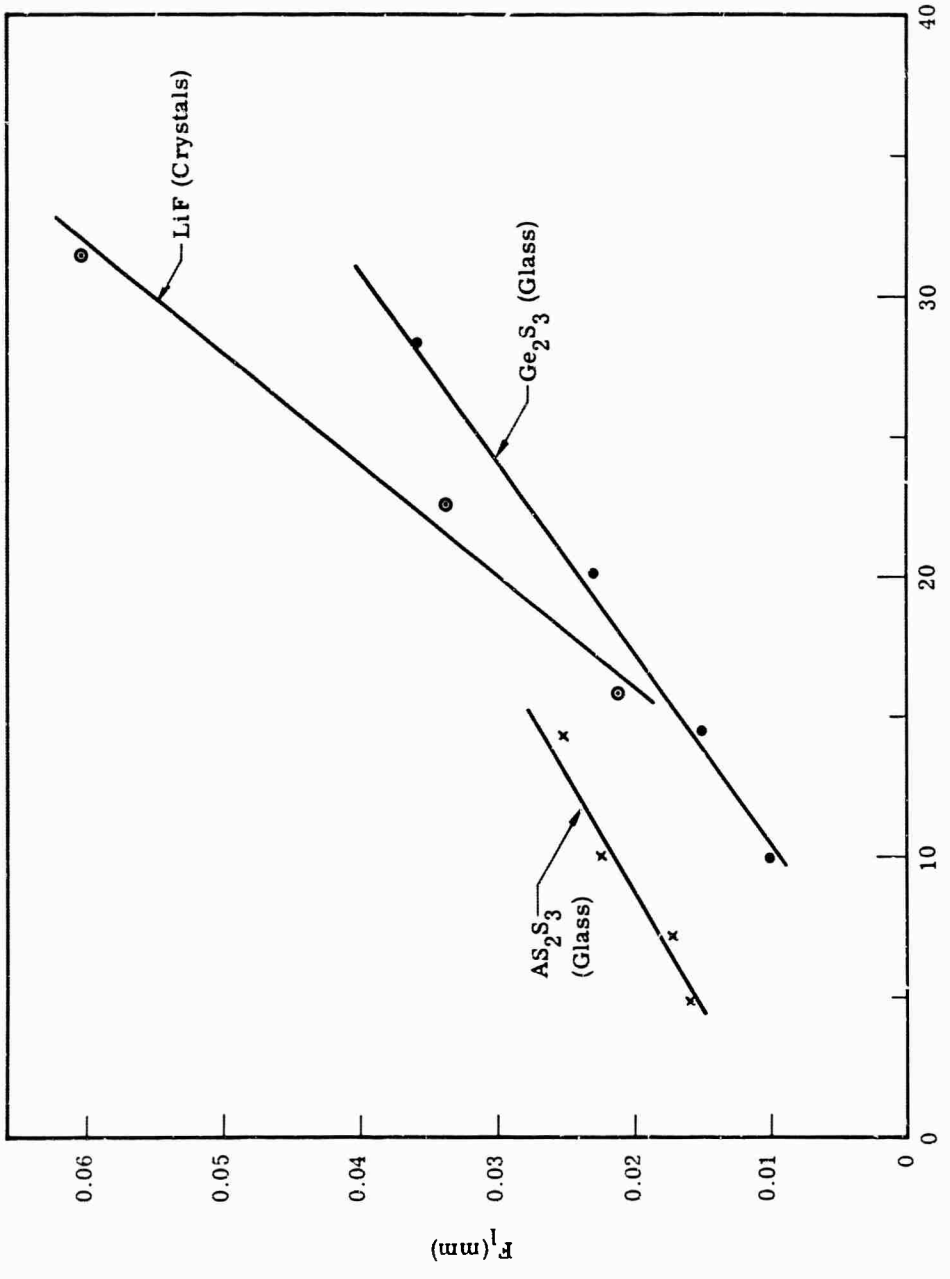


FIGURE 6. COMPARISON OF CURVES FOR FLAW LENGTH AND LOAD IN INFRARED GLASSES AND A SINGLE CRYSTAL

TABLE IV. CRITICAL STRESS OF FLAW FORMATION AND b-INTERCEPT VALUES IN INFRARED GLASSES AND A CRYSTAL

Material	Critical Stress σ_c (psi)	b-intercept (mm)
As_2S_3 — glass	5310	+0.009
Ge_2S_3 — glass	3410	-0.007
LiF — crystal	2570	-0.020

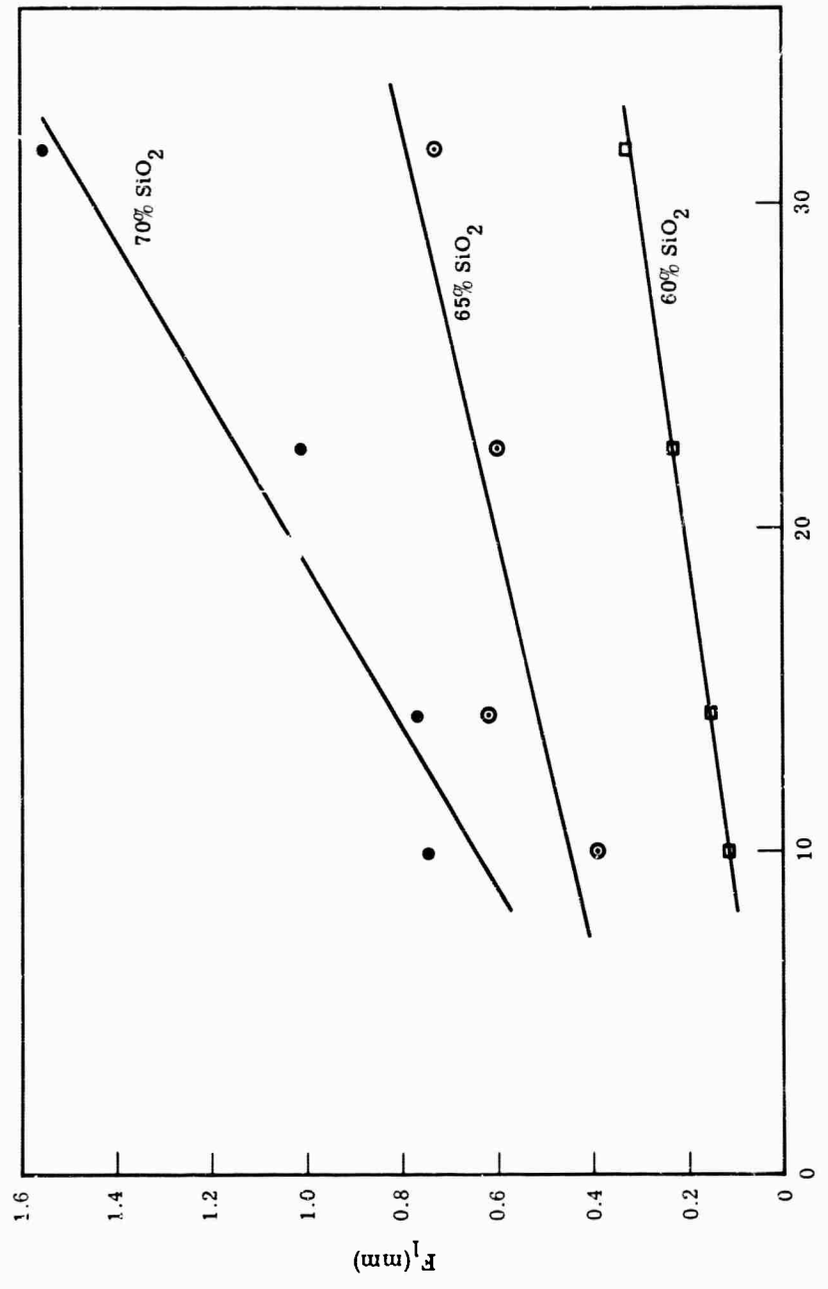


FIGURE 7. VARIATION OF FLAW LENGTH WITH INDENTER LOAD IN THE GLASSES REPRESENTING THE THREE LIQUID MODELS

stress as well as the b values which are related to the initial yield are presented in table V. The b value for the 60% SiO_2 glass representing the Frenkel-type liquid is very close to zero. This very low and in some cases negative b value is typical of systems containing ordered regions (see appendix). The Bernal or 65% SiO_2 system is intermediate in terms of critical stress and has a slightly higher b value than the 70% or Stewart system. The 70% SiO_2 glass representing a Stewart model with very long flaws also discloses a very low critical stress of flaw formation. The curves presented in figure 7 and the values listed in table V coincide very well with the predictions based on the unified theory of glass structure.

5.3. GLASS STRUCTURE RELATED TO RADIATION DAMAGE

The damage of solid materials by ionizing radiation involves a variety of processes, the simplest being the production of atomic displacement, broken bonds, and the formation of free radicals and color centers. Comparisons of the effects of radiation in ordered and disordered structures have been discussed by E. W. Elcock [9]. Elcock has stated that sufficiently long-time irradiations with neutrons or protons result in a noticeable destruction of an ordered structure, whereas a disordered structure discloses far less change for the same amount of radiation. The neutron irradiation of quartz crystals has been studied by Stevens, Strum, and Silsbee [10]. They reported that the exposure of crystalline quartz to neutron irradiation resulted in a rapid loss of long-range order and covalent bonds were ruptured. Recently it was reported that an OH^- formation occurs in a silicate glass when irradiated with high energy protons [11]. These various works were of interest in our investigations since we are examining subtle structural variations in different liquid systems. It appeared worthwhile, therefore, to explore the possible influence of irradiation on the glasses representing the three liquid models. Such a comparison represents one of the approaches we have used to correlate the flaw parameter data and our hypothetical liquid models with fundamental variations in the network properties of the different systems.

Before the current research project was initiated, the flaw parameter data indicated that the three soda-lime-silica glasses were very diverse systems although the possibility of their representing different liquid models was not recognized at that time. Because of the observed variations in flaw parameters, these glasses were subjected to a high dose of gamma radiation (10^6 rads at the rate of 1.1×10^5 rads/hr in a pile reactor). The flaw parameters were observed both before and after irradiation and although alterations were observed, the complete significance of these variations remained obscure. The N_b products both before and after radiation and the models representative of each system are listed in table VI. As noted in this table the 60% SiO_2 glass, or the Frenkel system, discloses the least change in N_b between the

TABLE V. CRITICAL STRESS AND b-INTERCEPT VALUES FOR THE THREE GLASSES REPRESENTING THE BASIC LIQUID MODELS. Soda-lime ratio 1.14 (wt percent)

Glass	Critical Stress σ_c (psi)	b-intercept (mm)	Liquid Type*
70% SiO_2	49	+0.25	Stewart
65% SiO_2	312	+0.30	Bernal
60% SiO_2	890	+0.01	Frenkel

*See appendix.

TABLE VI. INFLUENCE OF GAMMA IRRADIATION ON N_b PRODUCT IN GLASSES REPRESENTING THE LIQUID MODELS. Soda-lime ratio 1.14 (wt percent)

Glass	Control N_b	Irradiated N_b	Increase in N_b (%)	Liquid Type*
70% SiO_2	0.69	0.85	23	Stewart
65% SiO_2	1.00	1.27	27	Bernal
60% SiO_2	0.85	0.95	12	Frenkel

*See appendix.

radiated and nonirradiated glass. Since the unified theory of glass structure predicts that this glass represents ordered regions in a disordered matrix or considered overall as a heterogeneous or highly disordered system, this finding is consistent with Elcock statement [9] that irradiation could produce far greater damage in an ordered structure as compared with a disordered. In the case of the Stewart model (70% SiO_2 system) where we have long flaws forming over a fairly long-range degree of order, the radiation-induced change is much greater. From our model, the Bernal system would be expected to exhibit the maximum effect of radiation since it has the maximum degree of overall order (see appendix for nonfissured liquid), and this is confirmed in table VI data.

The changes in flaw length would certainly indicate that one could observe variations in strength between the irradiated and nonirradiated glasses (since higher N_b indicates higher strength values), and this possibility will be examined in future studies. This strength factor is also important since many infrared glasses used as optical elements are subjected to ionizing radiation in the space environments. Such a radiation environment could alter the strength characteristics over long periods of exposure. Radiation experiments have been conducted on infrared glasses [12]; however, the strength characteristics were not examined.

5.4. REFINEMENT OF THE LIQUID MODEL DIAGRAM

We have previously presented [1] a schematic diagram which we felt represented the changes in flaw parameters characteristic of three different liquid models (see fig. 9). In this case we considered the variations in both the flaw length and number when a given amount of network-modifying ion was substituted into the network. In a recent critical evaluation of the general unified theory of glass structure, it was pointed out that we might simplify this curve by representing the changes in the flaw characteristics as a ratio instead of plotting the simultaneous changes in both parameters. The original schematic diagram (fig. 9) was formulated after noting that typical changes occurred as network-modifying ions were added into a given base system (70% SiO_2). As the liquid structure changed from a Bernal to a Stewart liquid, a maximum in the flaw length and a minimum in the flaw number parameter occurred at the same point on the curve. The ratio F_l/F_n should, therefore, show this change in a more definite manner, that is, the effectiveness of a given ion in bringing about alterations from one liquid type to another would be enhanced. In figure 8, a number of network-modifying oxides substituted in a base system are shown. With the ions of high field strength the Stewart liquid is reached very rapidly with only a few moles substituted; whereas with the ions of weaker field strength, the maximum point or Stewart liquid is only reached after a greater number of moles are introduced into the network. The increase in the ratio in the case of SrO is currently being examined. With

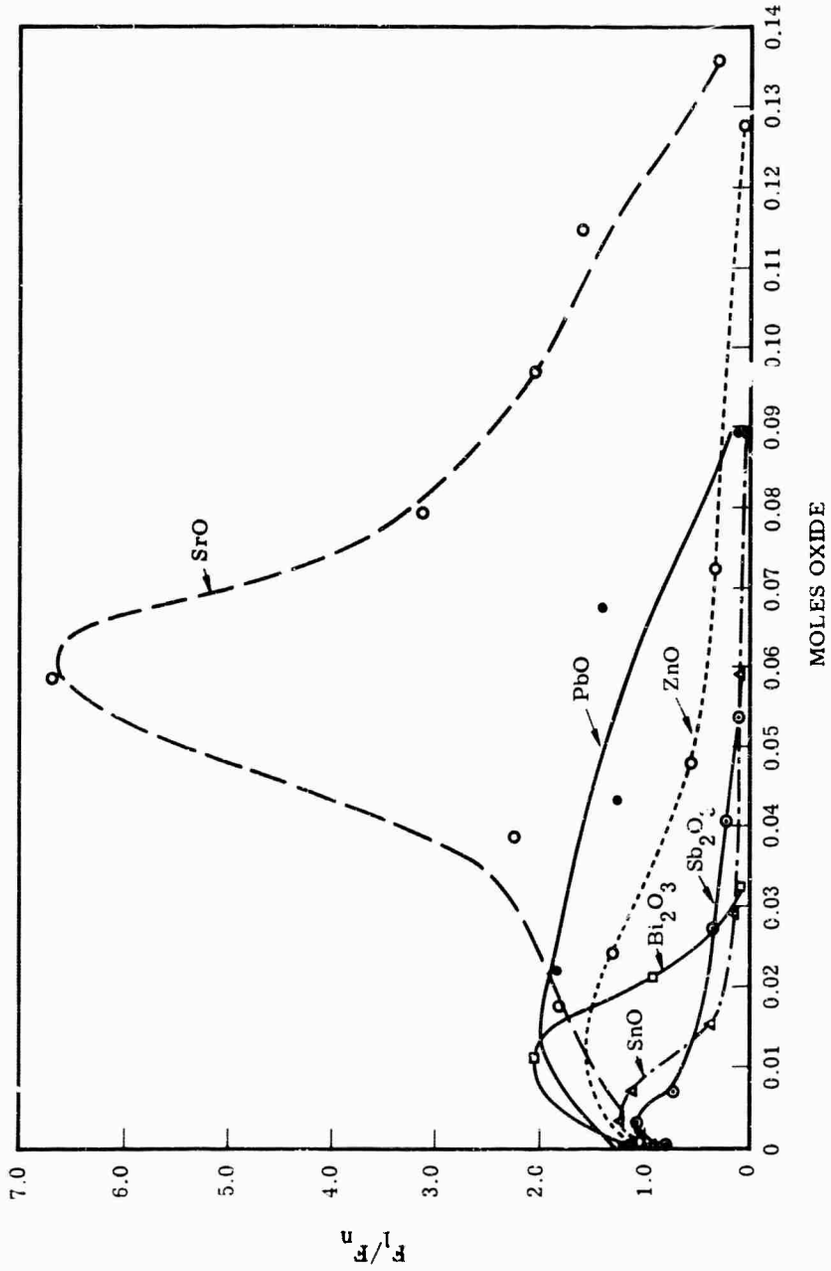


FIGURE 8. INFLUENCE OF VARIOUS NETWORK-MODIFYING OXIDES ON THE RATIO OF FLAW LENGTH TO FLAW NUMBER

additions made in a given system a plot of the ratio of flaw length to flaw number will very readily disclose how rapidly the liquid structure is changing and what particular model it represents.

6
CONTACTS WITH OTHER INVESTIGATORS

We have conversed with many scientists over the past six months, and the contacts with various establishments are listed here in chronological order:

(1) March 8, 1967: Phoenix Memorial Laboratory, The University of Michigan; Prof. J. M. Carpenter, Prof. D. H. Vincent, and J. Sutton

(2) March 13, 1967: Chemical and Metallurgical Engineering Department, The University of Michigan; Prof. L. VanVlack and Prof. T. Y. Tien

(3) March 24, 1967: Libbey-Owens-Ford Research Center, Toledo, Ohio; Dr. H. R. Swift

(4) April 4, 1967: Ford Scientific Laboratory, Dearborn, Michigan; Dr. M. E. Milberg

(5) May 1, 1967: 69th Annual Meeting of the American Ceramic Society, New York

(6) May 3, 1967: National Bureau of Standards, Washington, D. C.; G. Cleek

(7) May 18, 1967: J. Monk, E. Scheaffer, and P. Harget from the Owens-Illinois Technical Center, Toledo, Ohio visited our laboratory

(8) June 12, 1967: Materials Research Laboratory, Rensselaer Polytechnic Institute, Troy, New York; J. E. Neely

(9) June 13, 1967: Chemical Engineering Department, University of Rochester; Prof. G. T. Su

The knowledge gained from our visits to various laboratories was helpful in evaluating our theoretical model as well as our experimental efforts. The visits to the National Bureau of Standards and the Rensselaer Polytechnic Institute were especially rewarding. During the course of our discussion with Given Cleek (NBS) he suggested that we might profitably examine a possible correlation between liquidus temperature and the degree of ordering in the three soda-lime-silica systems used to represent our liquid models. This resulted in one of the predictions mentioned in section 4.5 of this report. The visit with J. Neely (RPI) was enlightening, since he is currently engaged in the study of diamond indentation behavior of fused silica. He confirmed our feelings that an examination of yield mechanisms in relation to changes in the basic glass network may contribute significantly toward our theory.

7
TENTATIVE AREAS OF FUTURE INVESTIGATIONS

In the following sections we have outlined important areas for future investigations where information is lacking and also areas which may prove fruitful in terms of altering and improving strength characteristics of infrared transmitting materials. These listed areas suggest directions of research which also have a high probability of predicting new composition regions and different methods of fabrication.

Studies of the empirical model of glass structure led to the discovery of a relationship between microelastic deformations in glass and its fundamental strength characteristics. As presented in a previous section of this report, a direct relationship was found between the load to fracture and microelasticity variations in a specific network. Future research will utilize this newly discovered important relationship. Now that we are able to explain wide variations in breaking stress in one particular glass sample, detailed studies of a given system or a family of glasses will become more meaningful. The distribution of structure-sensitive flaws in each glass system was shown to determine the slope of the linear curve relating the breaking strength to variations in microelasticity; therefore, the flaw studies will become an integral part of our research.

7.1. EXPECTED ACCOMPLISHMENTS DURING THE NEXT SIX MONTHS OF STUDY

We expect to concentrate heavily on investigations concerning the strength characteristics of non-oxide infrared glass systems. Samples prepared by American Optical and Texas Instruments Incorporated will be studied. Exploratory investigations will also be initiated to examine the effects of interstitial gases. This study will give us information concerning the effect of a specific gas on strength properties. With this information we will then be in a better position to recommend the type of gas to be added interstitially in the infrared systems.

Exploratory studies will also be initiated to examine the effects of irradiation on the strength of infrared transmitting glasses. The irradiation of these samples will be conducted at the Phoenix Memorial Laboratory at The University of Michigan. We also intend to examine the relationship of P_c to ϵ_{micro} in the three silicate glasses representing our basic liquid models. These data will clearly define the relationship between the liquid models and strength variations as predicted by our unified theory of glass structure. This will also establish whether or not the $1/F_n$ involvement in the slope of these curves is a linear or some higher order function.

7.2. RECOMMENDED AREAS OF FUTURE RESEARCH

7.2.1. INFLUENCE OF BONDED AND INTERSTITIAL GASES. As outlined in previous sections of this report, present studies indicate that bound water in the glass structure has a pronounced influence on strength characteristics of infrared transmitting glasses. Information is lacking or at best fragmentary on the structural influence of gases which enter the structure interstially; that is, they do not form bonds within the glass network. In the case of the fabrications of infrared glasses, inert gases such as nitrogen are often bubbled through the melt to eliminate the water band and the influence of this gas on strength has not been determined. From a few preliminary studies, it appears that gases other than nitrogen may be added which are more effective in terms of initiating a strength increase. In this phase of the study, we will, therefore, examine the effect on strength of both chemically-bound and interstitially-added gases within infrared vitreous materials.

7.2.2. RELATIONSHIP OF IRRADIATION TO STRUCTURE. As discussed in section 5.4, gamma irradiation can induce structural alterations in vitreous materials as determined by the surface flaw parameters. Such irradiation-induced alterations in structure will be examined in terms of their influence on strength and mechanical properties. In addition to gamma irradiation the influence of proton fluxes will also be examined. The effects of irradiation on infrared transmitting materials is important since these materials are exposed to intense cosmic rays, x-rays, etc. in extraterrestrial environments.

7.2.3. CHEMICAL PROPERTIES AS INFLUENCED BY SURFACE FILMS. The formation of surface films on optical elements offers one means of altering the strength characteristics. The newly found relationship between breaking strength and microelasticity offers one excellent test method for examining the influence of these surface films on the mechanical strength characteristics. The feasibility of using this technique was shown in figure 3 where a mechanically polished surface had entirely different slope characteristics or strength properties than a fresh breakage surface. These studies would be closely coordinated with an examination of transmission characteristics to determine the influence of surface coating on the optical properties.

7.2.4. INFLUENCE OF IMPURITY DOPINGS. Minute amounts of doping materials may be added in infrared glasses as is often done in the case of solid-state crystalline materials. The influence of a specific doping material on the mechanical strength characteristics would be examined by utilizing the relationship of P_c to ϵ_{micro}. The optimum concentration for a specific dopant would be determined by examining the slope change of these curves as a function of concentration. It would be expected that the maximum strength improvement would occur in the system disclosing the maximum slope value.

7.2.5. CONTACT WITH PRODUCERS OF INFRARED TRANSMITTING VITREOUS MATERIALS. We have contacted American Optical and Texas Instruments Incorporated to obtain samples of non-oxide infrared transmitting materials for use in our studies. These manufacturers have shown interest in our program and have offered to furnish us with samples covering a range of compositions and samples with various possible added gases and interstitial substitutions. This exchange of information between the laboratory and the manufacturer is important if the final outcome of the project results in improved strength characteristics in infrared transmitting materials.

8
SUMMARY AND CONCLUSIONS

Based on considerations brought forth during the initial formulation of a unified theory of glass structure, a direct relationship has been found between the breaking strength of glass and microelasticity. With this discovery, we are now able to completely account for the wide variations observed in the breaking strength within one given glass system. Heretofore, investigators have generally attributed large deviations in strength to unresolved factors such as surface contamination, scratches, etc. We have shown that these variations are due to differences in localized microelasticity within the glass network. Melting or dissolved gases in the glass were also previously predicted to have an influence on the strength of the glass. Results are presented which demonstrated that calcium-aluminate glasses melted in a vacuum have approximately twice the mean strength of glasses melted in air.

The strength-microelasticity relationship was also demonstrated to be closely related to surface flaw nucleation. The F_n parameter influences the slope of the linear curve obtained by plotting the breaking load P_c against the microelasticity ϵ_{micro}. This direct relationship between the breaking load and the microelasticity will be utilized to examine non-oxide infrared

systems, to compare the inherent strength of one system with another, and even to select regions of high strength in a given batch of optical glass.

A number of other predictions based on the unified theory of glass structure were made with regard to the structural characteristics of vitreous systems. Flaw formation was previously shown to be related to the liquidus temperature or crystallization potential within the glass. Since the F_n parameter was also taken to be related to nucleation centers, it was predicted that this parameter should be related to the liquidus temperature. The glasses representing the three liquid models were examined, and the published values of liquidus temperatures plotted as a function of F_n disclosed a direct correlation. The flaw involvement in the P_c vs. ϵ_{micro} relationship was also predicted to be quite different for two different surface states on a given glass sample. The commercially polished surface of plate glass was compared with the fresh breakage surface, and in both cases the P_c vs. ϵ_{micro} curves were linear but with markedly different slopes. These different slopes were the results of markedly different flaw nucleation characteristics on the two surfaces.

The unified theory of glass structure was utilized to examine both oxide and non-oxide infrared systems. Induced radiation effects in the three glasses representing the basic liquid models were different, and the variations were predicted from the liquid model theory. The critical stress of flaw formation was also shown to be markedly different in infrared glasses than for an infrared transmitting crystal. The liquid model system, therefore, readily distinguishes between a pure crystalline and a glassy state. Contacts were made with a number of other workers concerning our theory of glass structure, and in general the concept of flaw movement or flaw involvement in strength variation in vitreous systems received considerable interest and favorable comment.

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Appendix
THE THEORETICAL MODEL AND ITS APPLICATIONS

A.1. PRESENTATION OF THE THEORETICAL MODEL

A phenomenological theory which has been designated as the unified theory of glass structure is presented here for reference purposes. This theory introduces the concept of order-disorder transitions and liquid model transformations within a glass network and has been found to be useful in elucidating and predicting structural behavior in both oxide and non-oxide glass systems. The degree of order and the structural characteristics of a particular glass system may be represented by one of three existing models of liquid structure: Bernal, Stewart, and Frenkel. The unification of these three liquid models constitutes the basis of this theory.

Structure-sensitive flaws designed to facilitate the formulation of this network hypothesis have been utilized extensively in the studies. Based on experimental observations concerning the nature of flaw variations as various ions are substituted in the glass network, this theory agrees with the observed internal energy variations in a number of infrared vitreous systems. Tentatively, the unified theory may be briefly stated as follows:

> Vitreous structures tend to transform continuously from a network characteristic of one type of liquid structure to that of a different structure depending on the induced thermodynamic or compositional alterations. Under this unifying concept of liquid transformation, order-disorder transitions are examined and determination of whether a given structure is more closely represented by a Bernal, Stewart, or Frenkel type of liquid model is considered informative [1].

There is a need for this unified theory in consideration of order-disorder transformation because no well-defined model can be representative of all inorganic vitreous networks. The inherent problem of encompassing all of the various transitions in liquid structures is too great and a single model would be meaningless if the details of structural alterations in many diverse systems were to be accounted for. The three basic liquid models used to predict the ease with which a given structure may form a glass by rapid cooling are as follows (from ref. 1):

(1) Bernal "flawless liquid"—This is described as a structure approaching a perfect covalent crystal which is essentially free of flaws. With increasing thermal energy, this covalent structure gradually changes from a crystal to a liquid through decreased binding forces in the lattice.

(2) Stewart "orientable liquid"—This structure contains molecular arrays showing various degrees of order and orientation. With these long-oriented groupings glasses may readily form when the material is supercooled.

(3) Frenkel "fissured liquid"—This is the antithesis of the Bernal model and it is assumed that the liquid is permeated with large numbers of fissures or surfaces of broken submicroscopic bonds. These fissures are conceived of as having dynamic

characteristics in that they may close and form spontaneously. In glass a Frenkel would be represented by one having regions of a high degree of order imbedded in a matrix of lesser order, with the fissures forming between these phase transition regions.

Glasses may have molecular properties represented by all three types of these liquid models but in varying degrees. In each given system one type of model may be more characteristic of that particular liquid structure. Experimental evidence showing continuous changes in the liquid structure of glasses has been demonstrated in systems with ionic substitutions. A schematic diagram showing the changes in the flaw parameters with additions of network modifying ions into a base system is shown in figure 9 along with additional notations. Superimposed on this figure are indicated regions in which a particular liquid model is believed to be predominant. In figure 9, N represents the number of cations necessary to produce the maximum, M', in the flaw length curve. At this maximum, it is assumed that the structure is now of the Stewart type with the greatest number of long orientable structures and a minimum number of internal fissures indicated by the minimum in the F_n curve. As cation additions increase, the disruption of internal bonds become more frequent and the number of fissures drastically increases as shown by the rapid rise in the F_n curve. At the point designated by M_c in this figure, crystallization occurs and just preceding this we have a structure which is permeated with regions of high order with their associated fissures and therefore is of the Frenkel type. With substitutions of ions in the network, we may therefore alter the structure and develop characteristics typical of all three models of the liquid state.

A.2. APPLICATIONS OF THE MODEL TO DEFINE A PARTICULAR GLASS SYSTEM

There are several ways that this particular model of liquid structure may be applied to glass systems. The factors governing the applicability of this model are (1) the number of samples available covering systematic changes in ionic concentration within a given glass system and (2) the flaw parameter values within these systems. In the following brief outline discussing the detailed application of this model, we have gone from the ideal case of assuming that we have the proper number of samples and compositional information to the condition where only one sample is available without specific knowledge concerning its properties.

(1) In this hypothetical situation, we assume that from 10 to 20 samples are available with known systematic alterations in the ionic concentrations. In this case, the flaw parameters would be determined and plotted as a function of ionic concentration to determine the specific flaw characteristics (the type of curve as shown in fig. 9). With this established, we would then be able to predict those structures having the most mechanical stability in terms

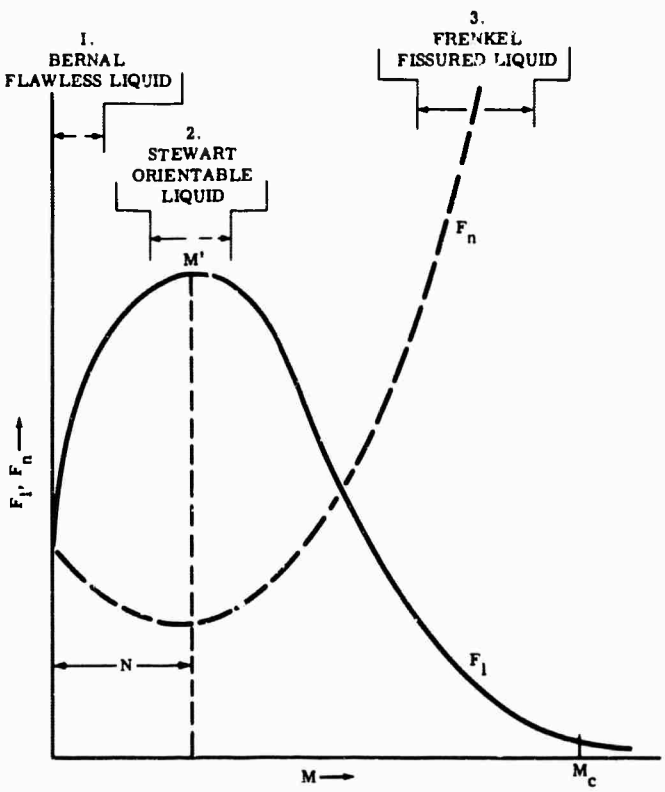

FIGURE 9. SCHEMATIC DIAGRAM SHOWING EFFECT OF NETWORK-MODIFYING SUBSTITUTIONS ON FLAW PARAMETERS. Three liquid model regions are designated.

of thermal and mechanical shock characteristics. Also with this type of diagram, we would be in a position to judiciously pick those glasses which might be more susceptible to alterations in structure by the addition of interstitial gases and impurities.

(2) In this case we have only a few samples, let us say a half dozen, of related composition but where no systematic alterations or substitutions have been made. The flaw parameter changes would be compared with others in the same basic system. In addition, it would be necessary to determine the load curve versus flaw length ($P^{1/2}$ vs. F_1) relationship for each of these systems. From the slopes and nature of these load curves, the individual systems could then be categorized in terms of a particular liquid structure.

(3) Given a single isolated sample of unknown characteristics but of known composition, here again we would want to obtain the $P^{1/2}$ vs. F_1 curve to categorize this particular system into a specific liquid model. In this case, it is somewhat more difficult to make predictions concerning improvement of structural characteristics but knowing the liquid structure would certainly give us a good start in predicting how structural changes might be brought about. In this case where we have only a single isolated sample, other properties such as crystallization temperature, microyield, etc. would be of advantage in making predictions concerning structural alterations.

The categorization of each particular glass system into the specific liquid model represented by its network characteristics is advantageous from the viewpoint of predicting its mechanical strength characteristics under field conditions. As more information is obtained, alterations in the structure such as introduced gases, ionizing radiation, etc. can be predicted with more certainty.

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13. ABSTRACT

Based on considerations of the important role of microyield in glass-structure studies, a linear relationship was found between the breaking strength of glass and microelasticity. This relationship disclosed that the wide spread observed in breaking strength values within one given glass system is due to localized variations in elasticity. Heretofore, these large deviations in strength have been attributed to unresolved factors such as surface contamination, handling defects, etc. Data presented demonstrate a spatial variability in microelasticity, the form of which determines the strength of glass under nonuniform loading conditions. The practical implications in terms of improving the mechanical properties of infrared glasses are discussed.

Several predictions suggested by a previously defined unified theory of glass structure are examined and they generally substantiate the fact that variations in the basic glass structure are determined by surface flaw parameters and flaw interactions. In particular, this study confirmed that gases bound within vitreous networks can influence mechanical strength.

The surface flaw characteristics and critical stress of flaw formation was determined both in infrared transmitting glasses and in a single crystal. The differences in the flaw parameter values for the crystalline solid and the glasses were as predicted. Induced radiation effects were examined in three glasses representing the basic liquid models, and the changes in flaw characteristics are interpreted in relation to liquid model theory.

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Breaking strength						
Microelasticity						
Flaw nucleation						
Liquid models						