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STRENGTH-STRUCTURE RELATIONSHIPS IN VITREOUS INFRARED MATERIALS

Final Report

1 April 1967 Through 31 March 1968

W. C. LEVENGOOD
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INFRARED AND OPTICAL SENSOR LABORATORY
Willow Run Laboratories
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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NOTICES

Sponsorship. The work reported herein was conducted by the Willow Run Laboratories of the Institute of Science and Technology for the Advanced Research Projects Agency, Washington, D. C., ARPA Order No. 269, Program Code No. 5730. Contracts and grants to The University of Michigan for the support of sponsored research are administered through the Office of the Vice-President for Research.

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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. 57[illegible]0, and monitored by the Office of Naval Research under Contract No. NONR 1224(57). Dr. Arthur Diness was the contract monitor. The following reports were issued for this project:

W. Wolfe and W. C. Levengood, Basic Structure of Infrared Glasses (Semiannual Progress Report, 1 August 1965 Through 1 February 1966), Report No. 7518-3-P, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, March 1966.

W. C. Levengood and T. S. Vong, Basic Structure of Infrared Glasses (Final Report, 1 August 1965 Through 31 December 1966), Report No. 7518-8-F, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, January 1967.

W. C. Levengood and T. S. Vong, Structural Relationships in Vitreous Infrared Materials (Semiannual Progress Report, 1 April 1967 Through 30 September 1967), Report No. 7518-10-P, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, November 1967.

ABSTRACT

Investigation of basic strength and structure relationships in vitreous materials revealed that a linear relationship existed between the inherent breaking strength and the microelasticity of the three glass systems which were examined, silicates, calcium aluminates, and arsenic trisulfides. Using this relationship, it is possible to explain the wide spread observed in breaking-strength data in terms of microelasticity variability and to utilize these linear curves to analyze subtle alterations in the basic structure and in the surface conditions of glasses. Regular polishing techniques as well as surface abrasion and mechanical damage produced quite drastic changes in the microelasticity characteristics of the glasses.

The effect of melting conditions was examined in arsenic trisulfides, and data are presented showing an increase in strength after a melting treatment designed to reduce optical absorption bands in the material. The importance of surface polishing in altering microelasticity characteristics was corroborated in the studies with arsenic trisulfides. Irtran materials were also examined. Irtran type #1 disclosed a structure more characteristic of a vitreous material than of a polycrystalline, which indicates that under certain conditions the hot press type of network may approach some degree of amorphism.

Data concerning the relationship between shear modulus values determined by sound-velocity measurements and the flaw parameters in the three basic systems are also presented.

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STRENGTH-STRUCTURE RELATIONSHIPS IN VITREOUS INFRARED MATERIALS

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INTRODUCTION

A program was initiated to examine the basic structural characteristics of infrared glasses more than two years ago. In the initial phases of the investigation, the general approach was to study variations in the internal bond energies of various glasses in an attempt to relate these variations to known liquid model theories. The data obtained in these early stages were organized into a unified theory of glass structure which was considered to have a phenomenological foundation [1].

The unified theory of glass structure was developed so that it could be applied to both infrared and noninfrared transmitting glasses. The advantage of this theory is that it points out the tendency of glasses to transform in a continuous manner from a network characteristic of one liquid structure to that of a different liquid structure depending on the thermodynamic or compositional alterations. Under this unifying concept of liquid transformation, order-disorder transitions are examined, and the type of liquid model (Bernal, Stewart, or Frenkel) which a given structure most closely represents is established. The details of the theoretical model are presented in modified form as an appendix to this report. Structure-sensitive surface flaws were used as a means of determining these variations in liquid structure quantitatively. It was shown experimentally that it was possible to place a given type of infrared glass within the framework of one of these three basic liquid models. Such a categorization was important because both the influence of various dopant materials on the structure and the strength characteristics under applied thermal or mechanical stresses could be predicted more judiciously if the liquid type was known.

This report describes the results of a year's study devoted to examining the relationship of strength to structure in vitreous infrared transmitting materials, with emphasis placed on the last six months' work. In the first half of this program [2], the unified theory of glass structure and other information obtained by utilizing the surface-flaw studies were applied to existing infrared glass systems, in particular to nonsilicate glasses such as calcium aluminates. It has been shown by the theory that the successful prediction of liquid models representative of various types of desirable compositions and structural alterations may lead to improvements in strength.

One of the most important discoveries which evolved from this study was that the spread, or large deviations, in strength data may be completely accounted for by considering the elastic yield mechanism at the point of load application. A linear relationship is obtained by plotting the load which causes fracture against the empirically determined value of microelasticity. Although the details of this discovery were presented in the semiannual report [2], the method and some of the implications of the original findings are reiterated here because of their importance in contributing to a more fundamental understanding of breakage processes in vitreous materials. It has been established that the linearity between breaking load and the value of microelasticity at the point of load application provides information concerning elastic yield variations in microregions of the glass network and clearly demonstrates that there is a spatial variability in the microelasticity, the form of which determines the ultimate resistance of glass to breakage under nonuniform loading conditions. This spatial microelasticity relationship has been examined in various infrared glasses, and it has been found very useful in defining strength capability in calcium aluminates as well as in nonoxide systems such as arsenic trisulfide. The microelasticity characteristics, which are sensitive to surface and melting conditions, can be quantitatively examined to determine their effect on strength levels. During the latter half of this project period, various structural alterations were examined to determine their possible utilization in improving the strength of existing nonoxide infrared systems.

In the execution of these efforts, we have discussed our findings with infrared glass manufacturers and users, and we have found that there is a great deal of interest in improving the strength and structural characteristics, particularly in the nonoxide systems. In this report results obtained from samples submitted by several manufacturers are discussed. A section concerning our association with Professor M. H. Manghnani at the University of Hawaii's Institute of Geophysics is also included. He has been examining the concepts outlined in the unified theory of glass structure and applying them in his studies of compressional and shear wave-sound velocities in glass.

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STRENGTH PROPERTIES AS RELATED TO INHERENT VARIATIONS IN MICROYIELD

As previously mentioned, the method of measuring localized strength and microelasticity will be briefly summarized here to provide continuity and to eliminate the need for referring to earlier reports which may not be immediately available. Strength tests were conducted under conditions of nonuniform loading or loading in a microregion, since the failure of most glasses in field situations occurs when nonuniform stresses are induced by either mechanical or thermal forces. The infrared glass material used in satellites and missiles offers an example of environmentally induced forces of a nonuniform nature. By contrast, most laboratory investigations are conducted under conditions of uniform loading, and such procedures tend to average out and deemphasize the influence of local variations in bond strength. Only a few cases have been reported where the strength of glass has been examined under nonuniform loading conditions. The method employed in one such study [3] was later used by Levengood [4] to demonstrate a direct relationship between the mean breaking load under localized loading conditions and the formation of linear flaws on fresh breakage surfaces. The discovery of this relationship provided the first direct evidence of the involvement of flaw formation with glass fracture processes.

One very puzzling aspect of this study was the very large spread in the strength data observed even though the tests were conducted on fresh fracture surfaces. Surface contamination and weathering products which normally contribute to large strength variations would not be a factor on the fresh surfaces. The persistence of large strength deviations on clean surfaces was one factor which led us to consider possible variations in microelasticity within the glass system.

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 those 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 which recorded the penetration of the sphere into the test sample as a function of the applied load.

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 DIRECT RELATIONSHIP BETWEEN MICROYIELD AND STRENGTH

In figure 1, we have diagrammatically represented the relationship between the steel sphere penetrating the glass surface and the curve plotted on the Instron tester. The deformation vs. 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 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 of the load test, then increases at a much slower rate with a continuously 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.

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 cracking 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 generally 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

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

We have used the symbol ϵ_{micro} to designate the microelasticity so that it will not be confused with E which normally designates Young's modulus of elasticity, a measure of yield in the bulk material.

It has been demonstrated [2] that a linear relationship is obtained by plotting the values of ϵ_{micro} as a function of the cracking load P_c. This was the first time that a mechanism explaining the pronounced scatter of breakage data within a given type of network has been placed on a quantitative basis. The importance of utilizing this method of examining the strength characteristics in various infrared glasses will be discussed in the following sections.

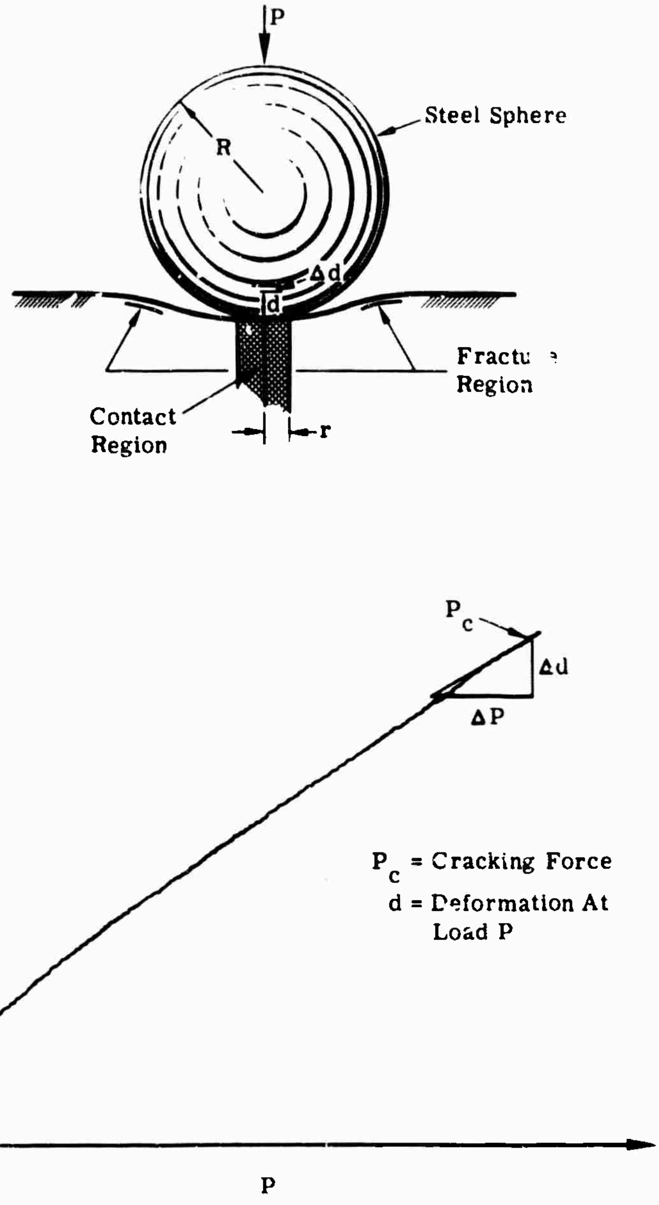

FIGURE 1. DIAGRAMMATIC RELATIONSHIP BETWEEN LOAD P AND LOCALIZED DEFORMATION d

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STRENGTH-MICROELASTICITY VARIATION IN NONOXIDE GLASSES

A relationship between strength and microelasticity was clearly shown to exist for quite diverse types of oxide systems. In order to determine whether this same type of relationship would be observed in nonoxide glasses, arsenic trisulfide glasses were studied.

3.1. STRENGTH-MICROELASTICITY RELATIONSHIP IN ARSENIC TRISULFIDE GLASSES

In our recent efforts to determine the P_c vs. ϵ_{micro} relationship in nonoxide infrared systems, two types of arsenic trisulfide glasses (submitted by the American Optical Company) were examined. Due to the lower order of fracture strengths in these materials, it was much more difficult to determine the exact load point at which fracture was formed. Unlike the silicate glasses or the calcium aluminates in which an audible click almost always occurs at the breaking point, the arsenic trisulfide glasses fractured with no measurable sound. The problem of locating the exact moment of fracture in these glasses was resolved solely by optical means. By applying an intense light source at the point of loading and a 50X microscope focused at the load point from underneath the test surface at a slight angle, the exact moment of fracture (not necessarily the Hertz cone fracture) was determined. Utilizing this somewhat unusual experimental approach in determining the P_c with the arsenic trisulfide glasses, ϵ_{micro} was then calculated in the usual manner (see sec. 2.2). The P_c vs. ϵ_{micro} curves were plotted for the two arsenic trisulfide glasses as shown in figures 2 and 3. These curves show that the same linear relationship between strength and microelasticity holds for the nonoxide systems as well as for the silicates and the calcium aluminates. We may now proceed to examine the nonoxide systems using this newly found relationship for determining spatial variability in the microyield properties.

3.2. EFFECT OF MELTING CONDITIONS AND SURFACE STATES ON STRENGTH CHARACTERISTICS

The samples of arsenic trisulfide glass which were submitted by the American Optical Company represent structures prepared under two different melting atmospheres. One sample designated type I was melted in its own atmosphere and the second sample designated type II was melted under special conditions. The exact nature of these special conditions is considered by the company as proprietary information; however, in general, special treatment is intended to reduce the waterband absorption at 2.8 μ. Our interest in these two glasses was to find out if different melting conditions would influence the mean strength and the slope characteristics of the P_c vs. ϵ_{micro} curves.

The data in figure 2 for the type I glass clearly demonstrate the presence of the linear relationship between breaking strength and ϵ_{micro} in the nonoxide glass for both the fractured

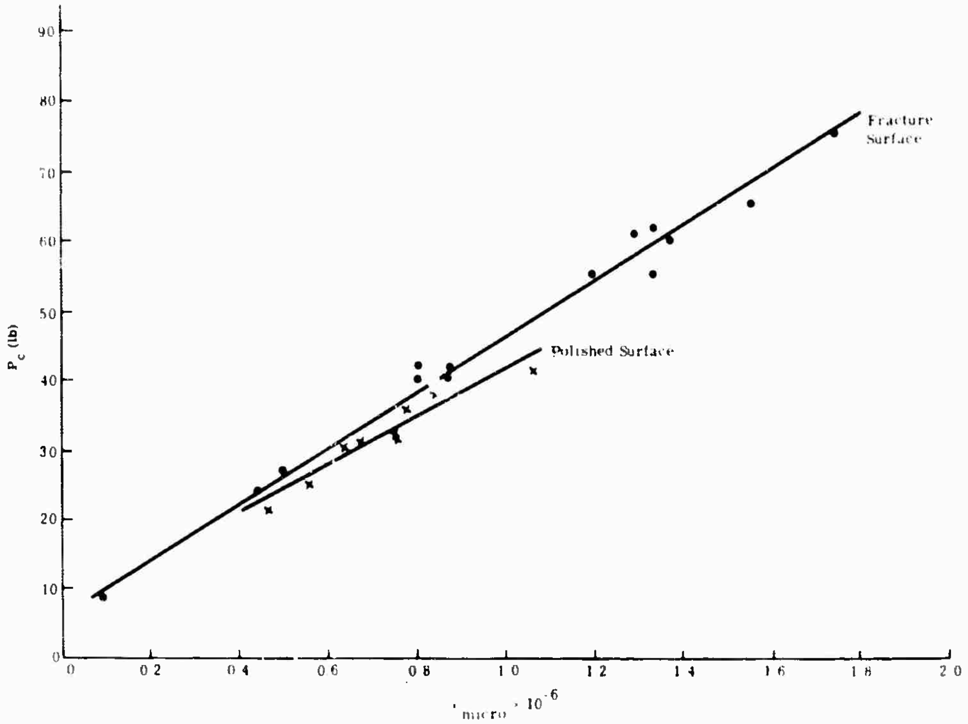

FIGURE 2. LINEAR RELATIONSHIP BETWEEN BREAKING LOAD P_c AND MICROELASTICITY ϵ_{micro} FOR DIFFERENT SURFACE CONDITIONS IN TYPE I ARSENIC TRISULFIDE GLASS

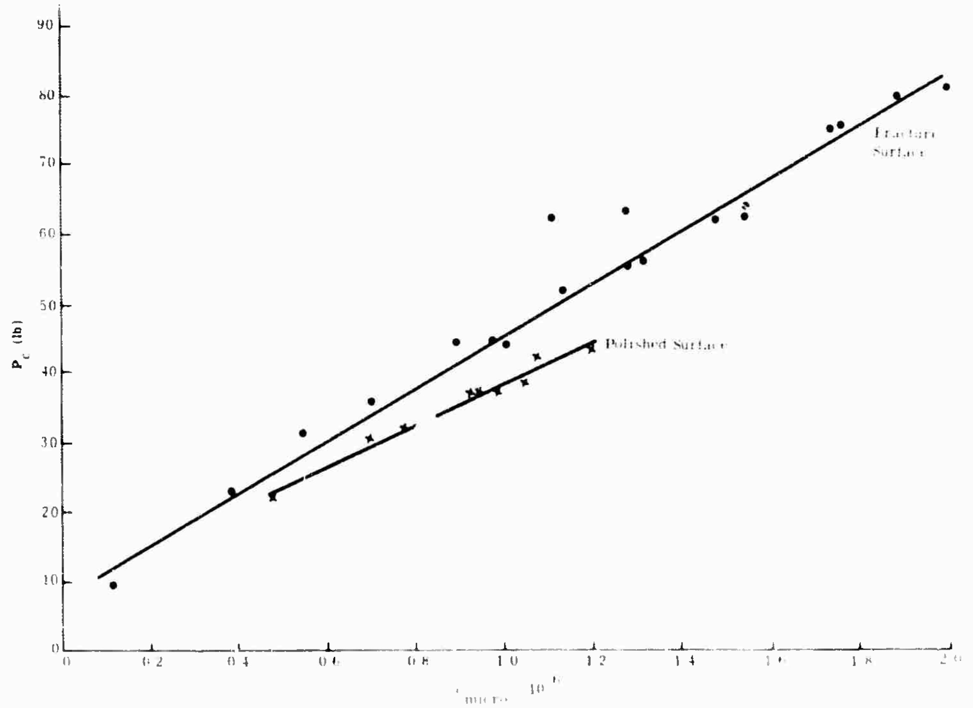

FIGURE 3. LINEAR RELATIONSHIP BETWEEN BREAKING LOAD P_c AND MICROELASTICITY ϵ_{micro} FOR DIFFERENT SURFACE CONDITIONS IN TYPE II ARSENIC TRISULFIDE GLASS

and polished surface. They also substantiate the difference in the microelasticity characteristics previously observed on breakage surfaces as compared with optically polished surfaces. Since the slope is of lesser magnitude on the polished surface, the previous findings obtained on ordinary plate glass are confirmed. The data for the type II glass are presented in figure 3 and again curves with two distinct slopes were obtained for the two types of surfaces. The mean breaking strengths for the curves shown in figures 2 and 3 are presented in table I.

TABLE I. BREAKING STRENGTH-MICROELASTICITY VARIATIONS IN TWO TYPES OF ARSENIC TRISULFIDE SAMPLES

Sample	Fresh Surface $\overline{P}_c$ (lb)	Fresh Surface Slope	Polished Surface $\overline{P}_c$ (lb)	Polished Surface Slope
Type I - Regular Melt	46.9	39.0	31.7	33.2
Type II - Special Melt	53.6	39.5	35.1	30.0

The data in table I demonstrate that both the fresh breakage and polished surfaces on the special-melt sample disclose higher mean strength than under the regular melt conditions. If the special melting does, as previously found in the calcium aluminates, remove OH groupings within the network, then this could account for the increased strength. These data also substantiate our previous prediction that melting conditions are of considerable importance in determining the mechanical characteristics of infrared glass networks.

3.3. ELASTIC YIELD VARIATIONS IN IRTRAN MATERIALS

Savage and Nielson in a recent publication on the properties of chalcogenide glasses [5] state that at present there appears to be negligible information concerning the mechanical properties of infrared glasses. Often the strength, yield, and cold flow properties of nonoxide infrared systems are expressed by Knoop hardness values. We feel that this does not represent a true strength parameter for glass or infrared materials, since Knoop hardness as determined by the diamond indentation does not readily discriminate between flow and fracture, and our studies have shown that these factors should be considered separately.

The differences between the fracture processes in polycrystalline or glass type materials become readily apparent when utilizing the localized strength test determinations produced by the Instron tester. An example of an unexpected behavior was shown in two types of Irtran materials submitted by Eastman Kodak Company. In Irtran types #2 and #5, the P_c strength determinations disclosed instead of the usual Hertz ring fracture found in glassy materials a radial type of crack pattern more characteristic of brittle polycrystalline materials. In contrast, the structure of Irtran type #1 disclosed a typical Hertz ring fracture which is characteristic of a more vitreous structure. These two variations in fracture types are shown in figure 4 and demonstrate quite clearly the different responses of these structures to applied stress. This difference was also clearly manifested in the load vs. deformation curves, and although not enough values were obtained for a high degree of statistical significance, a glassy type of Irtran appeared to be of higher strength than the Irtran types #2 and #5 which showed the radial type of fracture pattern. It appears that in the fabrication of the Irtran materials, a possibility exists of preparing a structure more characteristic of an amorphous system than a polycrystalline. By carefully examining the parameters of temperature and pressure and by comparing these with the microelasticity properties, an amorphous type of network might result with a much greater degree of mechanical stability.

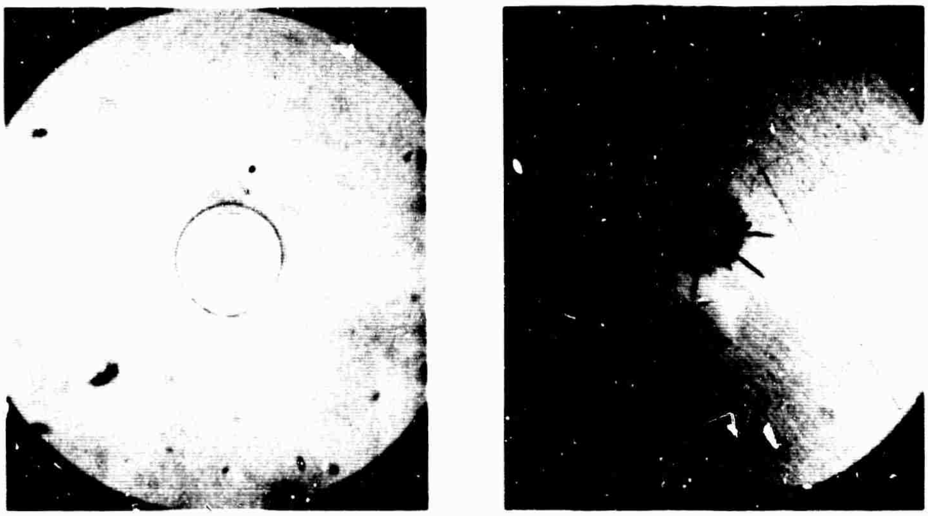

FIGURE 4. VARIATIONS IN FRACTURE PATTERN BETWEEN TWO IRTRAN MATERIALS

3.4. COMPARISON OF INDENTATION STRENGTH WITH MODULUS OF RUPTURE DATA

With the discovery of the linear relationship between P_c and ϵ_{micro}, the question arose concerning the relationship between the localized indentation strength and the tensile strength or rupture modulus as determined by the usual three-point loading techniques. It was previously demonstrated [2] that the rapidly formed indentation fracture value P_c is related to the rate of slow fracture in glass; however, this slow fracture parameter is also somewhat different than the strength value as determined by the usual tensile strength test. We have at the present time determined the mean indentation strength $\bar{P}_c$ values within three different types of glass systems, one of which was the nonoxide arsenic trisulfide. It is interesting to note that the $\bar{P}_c$ values determined in our laboratory are related to tensile strength values obtained from the published literature. The comparisons are shown in table II. The values for tensile

TABLE II. RELATIONSHIP BETWEEN INDENTATION STRENGTH AND TENSILE STRENGTH

Type of Glass	Tensile Strength σ (mean values, psi)	Mean Indentation Strength $\overline{P}_c$ (lb)	Ratio σ/P_c
Sheet glass	~7000	268.7	26.0
Plate glass	~5500	210.2	26.2
Arsenic trisulfide	~ 850	35.0	24.3

strength measurements were obtained from two independent sources [6, 7], and testing was carried out under diverse conditions.

The ratio of the fracture strength values to the indentation strength is roughly constant for these three vitreous networks. The value of 35 lb was chosen for the mean indentation strength of arsenic trisulfide since this is a value representative of the strength of polished surface (see table I). In the tensile strength tests, the polished surface would also be the surface examined. Although more studies would have to be conducted to validate unequivocally the constancy of this factor in other types of glass systems, it appears from this cursory study that indentation strength is, indeed, related to the mean tensile strength values. The advantage of using the indentation strength is that one can explain point-to-point variations in strength, and as a result the data become more meaningful in terms of structure and surface alterations.

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RELATIONSHIP OF SHEAR MODULUS VALUES TO FLAW PARAMETERS

In addition to utilizing the unified theory of glass structure in our studies of elastic yield properties in nonoxide systems, we have also applied this theory to a somewhat different area. Professor M. H. Manghnani at the University of Hawaii's Institute of Geophysics read some of our published work and became interested in the flaw parameter data as it applies to his studies of natural geophysical glasses such as obsidian. After seeing our analysis of the three basic glasses [2], which represent the different liquid models, Professor Manghnani contacted us to obtain samples of this glass for his study. His geophysical work consists of the determination of compressional and shear modulus values based on the measurement of sound velocities. The sound velocities are determined as a function of hydrostatic pressure applied to the specimens.

After submitting the samples which were requested, data were obtained from Professor Manghnani listing the sound velocities and the calculated shear modulus values in these three different systems. It is interesting to examine these data in terms of our unified theory of glass structure. The shear modulus data for these glasses are listed in table III along with the flaw parameters.

TABLE III. COMPARISON OF SHEAR MODULUS DATA WITH FLAW PARAMETERS IN THREE GLASSES REPRESENTING THE BASIC LIQUID-MODEL SYSTEMS

Type of Glass	Shear Modulus (kb)	N_b	F_1 (mm)	F_n (flaws/mm)
60% SiO_2	318	0.852	0.166	5.13
65% SiO_2	291	1.000	0.592	1.96
70% SiO_2	276	0.691	0.909	0.76

It is obvious from the data in table III that the shear modulus values do not correlate with the N_b product. On the other hand, the values of N_b (the product of F_1 and F_n) have been shown to be directly correlated with the mean breaking strength $\overline{P}_c$ values in these glasses. The shear modulus values would not be expected to correlate with strength since they represent bulk yield rather than bond strength in localized regions. Both the flaw length F_1 values and flaw number F_n values in table III do show a direct relationship with the shear modulus measurements as shown in the data plotted in figure 5. This relationship agrees very well with our previous hypothesis that both parameters are directly related to the extension or yield of

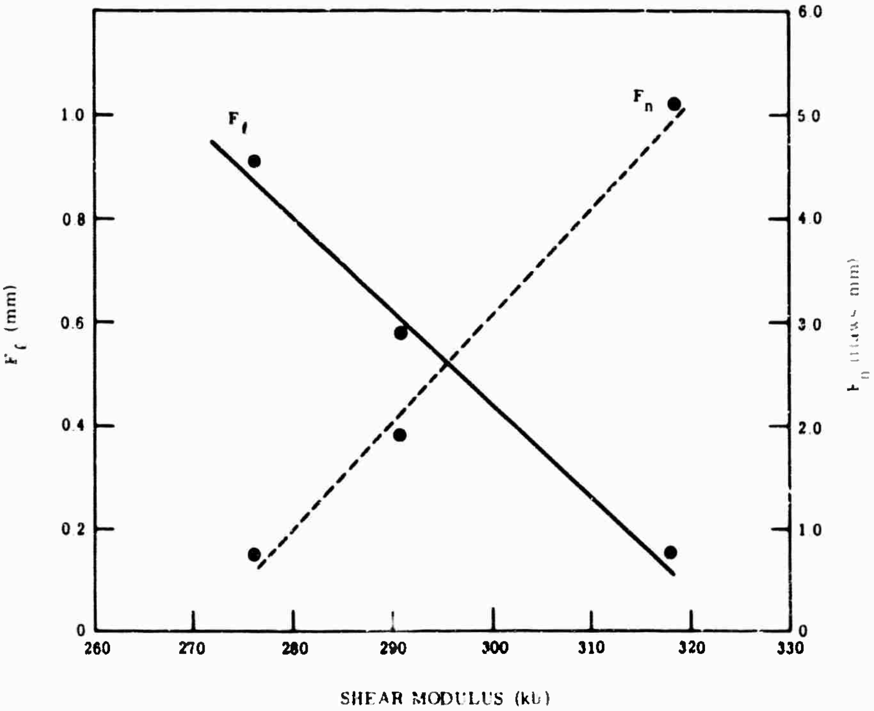

FIGURE 5. DIRECT RELATIONSHIP BETWEEN SHEAR MODULUS MEASUREMENTS AND FLAW PARAMETERS

the network and the distribution of ordered regions. In a glass with a very high shear modulus, the F_i value would be expected to be low and F_n high, indicating that the flaws cannot linearly propagate as far through the structure without being disrupted by some ordered region as they would in the case of a system with a low shear modulus. The glass demonstrating the highest shear modulus is the system represented by the Frenkel model. This glass has been characterized as having numerous regions of very high order imbedded in a matrix of lesser order. The shear modulus would be expected to increase with the degree of order in the system.

The data from Professor Manghnani constitute an independent confirmation of our theories and concepts concerning liquid structure and relate these findings to investigational efforts in a different area of research. Density measurements on these glasses also show a correlation with the shear modulus, that is, the highest density glass occurred in the Frenkel system. This was not unexpected since this glass possesses the high ordered regions and would be expected to be far more dense than the Stewart system with long, orientable, chain-like structures and a low degree of internal order.

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SUMMARY AND CONCLUSIONS

In this report, discussion of the strength and structure characteristics of infrared glass systems has included several factors which may be useful in improving the characteristics of existing commercial glasses. A newly discovered relationship between the breaking strength of glass and microelasticity was utilized to considerable advantage in examining the quantitative aspects of various strength and structure properties. This new method involves consideration of the differences in microelasticity within the glass network. Its advantage lies in the fact that deviations in strength are accounted for and that variations in microelasticity induced by surface treatments are quantitatively examined.

The conditions under which glass is melted were shown to be an important factor in variations of strength and elasticity. Comparisons of calcium aluminates melted in air and in a vacuum were shown to produce quite different effects on the strength and elasticity; vacuum melting reduced defect centers and the inherent strength was increased. This influence of melting conditions was shown in a specially melted sample of arsenic trisulfide glass, and the linear relationship between breaking strength and microelasticity was confirmed. The microelasticity characteristics of the fresh breakage surfaces on the arsenic trisulfide glasses were quantitatively quite different from those of the polished surface; this again confirms previous studies in the oxide systems. The type of polish and the treatment of the surface quite drastically alters the strength-microelasticity relationships.

Our hypotheses concerning the theoretical model (see app.) were applied in a somewhat different manner by Professor Manghnani at the University of Hawaii's Institute of Geophysics. He examined samples representing our three liquid model systems and determined the shear modulus by sound velocity techniques. These shear modulus measurements were found to correlate directly with the flaw number and flaw length parameters as expected from our liquid model theory. They did not correlate with the N_b product or the mean strength of these glasses. This study was important in the sense that it confirmed our thinking regarding the importance of the flaw parameters in defining the extent of yield or the extent of linear flaw formation in a given type of network and the degree of order.

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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 6 along with additional notations. Superimposed on this figure are indicated regions in which a particular liquid model is believed to be predominant. In figure 6, 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

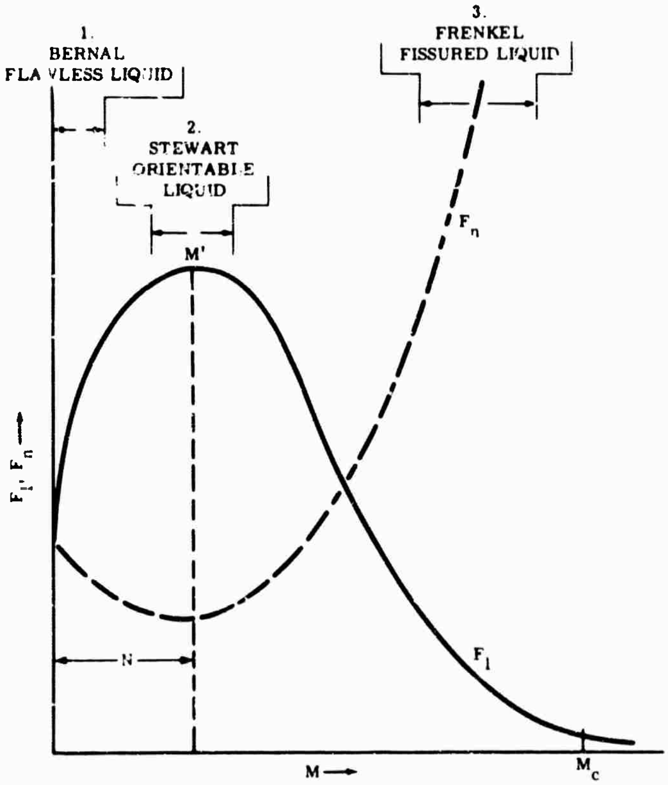

FIGURE 6. SCHEMATIC DIAGRAM SHOWING EFFECT OF NETWORK-MODIFYING SUBSTITUTIONS ON FLAW PARAMETERS. Three liquid model regions are designated.

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. 6). With this established, we would then be able to predict those structures having the most mechanical stability in terms 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 vs. 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

Investigation of basic strength and structure relationships in vitreous materials revealed that a linear relationship existed between the inherent breaking strength and the microelasticity of the three glass systems which were examined, silicates, calcium aluminates, and arsenic trisulfides. Using this relationship, it is possible to explain the wide spread observed in breaking-strength data in terms of microelasticity variability and to utilize these linear curves to analyze subtle alterations in the basic structure and in the surface conditions of glasses. Regular polishing techniques as well as surface abrasion and mechanical damage produced quite drastic changes in the microelasticity characteristics of the glasses.

The effect of melting conditions was examined in arsenic trisulfides, and data are presented showing an increase in strength after a melting treatment designed to reduce optical absorption bands in the material. The importance of surface polishing in altering microelasticity characteristics was corroborated in the studies with arsenic trisulfides. Irtran materials were also examined. Irtran type #1 disclosed a structure more characteristic of a vitreous material than of a polycrystalline, which indicates that under certain conditions the hot press type of network may approach some degree of amorphism.

Data concerning the relationship between shear modulus values determined by sound-velocity measurements and the flaw parameters in the three basic systems are also presented.

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