

DETERMINATION OF THE YIELD STRESS OF BOROSILICATE GLASSES BY MEANS OF SPHERICAL NANOINDENTATION

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Benjamin Lyle Hackett
August 2019

DEDICATION

To family, near and far, for their unwavering support

ACKNOWLEDGEMENTS

I am incredibly fortunate to be surrounded with such supportive and brilliant people. This work truly would not have been possible without the thoughtful guidance and insight from both Dr. George Pharr and Dr. Andy Wereszczak. Together they formed a terrific and indispensable pair.

For all of the technical support I received, I would like to thank Oak Ridge National Laboratory's Michael Lance, Shirley Waters, Tom Geer, Randy Parten, and Jamie Molaison. They helped with FTIR assistance, technical coordination, polishing support, specimen machining, and access to and training on a pressure cell respectively. I would also like to extend my gratitude to Brian Oisted for all the time spent on pressure and density measurements. I also would like to thank US Army Research Laboratory's Parimal Patel and Steve Kilczewski for fabricating the glasses studied here. Dr. John Dunlap's support at the microscopy facility of JIAM was invaluable. I'd also like to acknowledge the collaboration with UAB's Katie Ham and Dr. Yogesh Vohra that stimulated productive exchange of ideas and information. I'm also grateful for the training and access to their Raman instrument.

Thank you to my other committee members, Dr. Claudia Rawn and Dr. Chad Duty for their time and seasoned input. Although the lab eventually grew quiet, I want to acknowledge those that formed Dr. Pharr's group during my time in Knoxville and created a great working environment: Brittnee, Robert, and Ryan.

This work was supported for funding at the University of Tennessee, Knoxville from the US Army Research Office project W911NF-15-1-0614 under the direction of Program Manager David Stepp.

ABSTRACT

From the advent of mechanical tests conceived to measure material deformation characteristics by pressing an indenter into a surface, the desire to relate the *prima facie* quick and simple test back to more traditional testing methods and common material mechanical properties has persisted. For brittle materials, a particularly pernicious property to measure using conventional means is the yield stress, often neglected entirely in favor of fracture stress. Nevertheless, the yield stress is still an essential property necessary to describe the initial deformation of brittle materials, such as the response to a ballistic impact. The yield stresses of a suite of three very low alkali sodium borosilicate glasses, candidates for transparent armor, were determined by means of a novel methodology involving spherical nanoindentation. A theoretical description of this new method is provided alongside corroboration with uniaxial compression tests. The practical effect of water interaction during mechanical surface preparation of the glasses on measuring indentation-derived mechanical properties was analyzed. Connections between differences in yield stress for the three glasses were established on the basis of compositional and structural features elucidated through vibrational spectroscopy. The inclusion of high pressure double toroid diamond anvil cell compression of the glasses allowed extension of the yield stress analysis and correlated structural elements to instances of permanent compaction, a common deformation mode of amorphous materials. Together, this work represents a comprehensive inquiry into the nature of the yield stress for three borosilicate glasses and a process by which the yield stress itself may be determined using spherical nanoindentation.

TABLE OF CONTENTS

CHAPTER I: INTRODUCTION	1
CHAPTER II: OVERVIEW OF BOROSILICATE GLASS STRUCTURE AND INDENTATION DEFORMATION CHARACTERISTICS	5
Glass Structural Characteristics.....	6
Silicate	6
Borate	7
Borosilicate	7
Composition of Materials	9
Mechanical Deformation Modes of Glass	12
Elastic deformation	12
Densification	14
Plastic deformation	15
Theoretical Underpinnings of Indentation of Glass.....	17
Historical development of indentation theory	17
Indentation deformation of normal and anomalous glass	18
CHAPTER III: EXPLICATION OF A NOVEL TECHNIQUE TO ESTIMATE YIELD STRESS USING SPHERICAL INDENTATION	21
Background and Motivation for Developing New Method.....	22
Rationale for using spherical indentation.....	23
Comparison to extant methodologies	23
Advantages of newly devised method	24
Theoretical Description of the Methodology	25
Practical Considerations Necessary for Accurate Determination of Yield Stress.....	33
Selection of indenter radii size	33
Determining the true dimensions of the indenter	36
Verifying indenter area of contact.....	40
Frame stiffness and area function calibration	43
Loading rate	43
Application of the yield stress determination method to fused silica and soda-lime silicate glass.....	44
Materials and experimental details	44
Result of method application	45

Repeatability and error analysis	53
Discussion of Theoretical Assumptions	53
Tip defects	55
Frictional influences	55
Pre-existing stresses	55
Sample surface roughness	56
Choice of yield criteria and mechanisms	56
Apparent deformation	56
Insensitivity to small-volume elastic modulus changes	56
Testing the Veracity of the Method	57
Materials and experimental details	57
Results and discussion of veracity tests: BMG and tungsten compression	58
Titanium compression	67
Conclusions	71
CHAPTER IV: EFFECTS OF THE PRESENCE OF WATER DURING SAMPLE SURFACE PREPARATION ON THE MEASUREMENT OF NANOMECHANICAL PROPERTIES OF BOROSILICATE GLASSES	73
Glass Hydration Overview	75
Experimental Procedure	76
Materials	76
Surface preparation	76
FTIR	76
Nanoindentation	77
Electron microscopy	77
Results and Discussion	78
Elastic modulus and hardness	78
Porosity	81
FTIR spectra and borosilicate-water interaction	84
Conclusions	87
CHAPTER V: YIELD STRESS DETERMINATION AND STRUCTURAL RELATIONS TO THE HIGH-PRESSURE MECHANICAL RESPONSE OF BOROSILICATE GLASSES	88
Yield Stress and Composition	89
Structural characterization from FTIR spectroscopy	96
Structural characterization from Raman spectroscopy	98

Conclusions	100
Yield Stress and Densification from High Pressure DTDAC.....	101
Density changes	101
Effect of DTDAC testing on yield stress and other mechanical parameters	104
Structural characterization of densified glass using Raman spectroscopy.....	114
Conclusions	116
Process of Discovery of Yield Surface Boundary	116
CHAPTER VI: CONCLUSIONS	121
LIST OF REFERENCES	124
VITA.....	131

LIST OF TABLES

Table 2.1: Molar Composition of Each Studied Glass	8
Table 2.2: Compositional Molar Ratios and Poisson Ratio from Resonant Ultrasonic Spectroscopy	10
Table 3.1: Yield Stress Estimated Using New Technique.	52
Table 5.1: Yield Stresses for Three Borosilicate Glasses Determined Using New Spherical Indentation Method	94
Table 5.2: Mechanical Properties and Density of Pressurized Glasses	95

LIST OF FIGURES

Figure 2.1: The K and R ratios of each of the three glass compositions allow for their placement on this established structural model of SiO_2 - B_2O_3 - Na_2O glass from Yun Bray and Dell [22][23] establishing N_4 , the decimal fraction of boron that is tetrahedrally coordinated.	11
Figure 2.2: Composition triangle of the three glasses studied in depth in this work absent the small (~ 1 mol%) alumina contribution.	13
Figure 2.3: Permanent densification versus pressure curves of fused silica compressed in three different media that transmitted different amounts of shear from [29]. $A > B > C$ in terms of the magnitude of the shear. Higher shear components depress the threshold pressure necessary for densification to proceed. 100kb = 10GPa	16
Figure 3.1: Illustrative load-displacement curve of a material exhibiting loading-unloading hysteresis from non-recovered deformation and corresponding residual depth, h_f . Stiffness is taken as the instantaneous slope of the unloading curve at the peak load.	26
Figure 3.2: Schematic representation of S^3/P as a function of the displacement of an indenter into a surface. The effect of two different approaches to calculating the stiffness in S^3/P is shown. The dynamic unloading stiffness (solid line) is found by continuous stiffness measurement, while the loading stiffness (dotted line) is found using the slope of the loading curve. The two lines overlap in the perfectly elastic regime. The onset of permanent deformation is indicated when the two approaches to calculating S^3/P diverge.	30
Figure 3.3: Schematic depiction of rigid spherical elastic contact with a flat surface	31
Figure 3.4: The elastic shear stress field developed beneath the contacted surface during spherical indentation. Lighter shades indicate higher shear stresses. The maximum shear stress for $\nu = 0.18$ occurs at a relative depth of $z/a \approx 0.44$ where $r/a = 0$	34
Figure 3.5: The elastic hydrostatic stress field developed beneath the contacted surface during spherical indentation. Lighter shades indicate higher shear stresses. The maximum hydrostatic stress occurs at the center of the surface.....	35
Figure 3.6: Dynamic amplitude of oscillation versus depth of indenter displacement for fused silica using the $3.2 \mu\text{m}$ radius tip. The target held amplitude is 3 nm. Values derived from the S^3/P are dubious prior to reaching 100 nm because of the rapidly changing amplitude.	37

Figure 3.7: Swaths of accessible mean contact pressure and effective modulus pairs for the 50 mN actuator with a 50 nm low detectability floor. The swaths are color-coded according to the radius size of the indenter. The yellow diamonds mark the materials tested in this work.	38
Figure 3.8: Swaths of accessible mean contact pressure and effective modulus (Equation 3.2) pairs for the 1000 mN actuator and with a 50 nm detectability floor. The swaths are color-coded according to the radius size of the indenter. The yellow diamonds mark the material used in this work. If the diamond falls within a color-shaded region, elastic to plastic transition should be in the detectable range.	39
Figure 3.9: SEM image of the nominally 14 μm radius tip demonstrating that the overlaid sphere radius does not necessarily accurately represent the true curvature of the tip.	41
Figure 3.10: A fitted load versus displacement curve shown for fused silica indented with the nominally 5 μm radius establishes a correct description of the tip geometry. The brown curve is the actual load and displacement data, while the blue curve is based on a least squares power law fit of the data outlined in black and bounded by the two vertical dashed lines.	42
Figure 3.11: Spherical load-displacement curves of fused silica at peak loads ranging from ± 10 mN to 40 mN showing development of hysteresis as the peak load is progressively increased beyond a critical load.	46
Figure 3.12: (a). S^3/P parameter for nine 3.2 μm indentation tests of fused silica plotted simultaneously for each stiffness source: continuous stiffness measurement (brown) and loading curve interpolation (black). (b). A single indentation test taken from one of the nine samples. ± 10 nm uncertainty bounds are applied at the point of yielding.	47
Figure 3.13: Figure 3.13: (a). S^3/P parameter for five 8.6 μm tests of fused silica plotted simultaneously for each stiffness source: continuous stiffness measurement (brown) and loading curve interpolation (black). (b). A single indentation test taken from one of the five samples. ± 10 nm uncertainty bounds are applied at the point of yielding.	48
Figure 3.14: (a). The parameter S^3/P versus displacement is plotted using nine separate 3.2 μm spherical indentations of soda-lime silicate using dynamic continuous unloading stiffness (yellow, rising after divergence) and stiffness derived from the slope of the loading curve (black, falling after divergence). The point of divergence indicates the depth of penetration where yielding initiated. (b). A single test out of the nine is shown with ± 10 nm dashed uncertainty range about the yielding onset point.	50

Figure 3.15: (a). The parameter S^3/P versus displacement is plotted using nine separate 8.6 μm spherical indentations of soda-lime silicate using dynamic continuous unloading stiffness (yellow, rising after divergence) and stiffness derived from the slope of the loading curve (black, falling after divergence). The point of divergence indicates the depth of penetration where yielding initiated. (b). A single test out of the nine is shown with ± 10 nm dashed uncertainty range about the yielding onset point.	51
Figure 3.16: (a). Multiple load versus depth of indenter displacement curves for fused silica demonstrating high repeatability and low variance between tests. (b). Multiple dynamically-sourced S^3/P curves showing the level of noisiness of the parameter.....	54
Figure 3.17: Spherical load versus depth of indenter displacement curve for Vit 106a BMG using an 8.6 μm radius tip. Elastic behavior prevails right up until the 270 nm mark where there is the first pop-in, a brief burst of discretized plasticity.	60
Figure 3.18: S^3/P spherical indentation versus depth of indenter displacement for Vit 106a BMG using an 8.6 μm radius tip. Two means of obtaining stiffness are showcased, and their divergence indicates the initiation of plasticity at the pop-in depth. The spike downwards of the interpolated loading stiffness curve (black) is an artifact discontinuous jump in displacement and the interpolation process.	61
Figure 3.19: SEM micrograph of a 100 mN spherical indent on Vit. 106a BMG using an 8.6 μm radius round diamond tip. Multiple shear bands are seen accommodating plastic flow.	62
Figure 3.20: Compressive uniaxial loading of Vit 106a. Stress versus an uncorrected strain is displayed along with a horizontal dotted line marking the first discernable deviation away from linearity, the elastic limit, which is taken to be the yield stress.	63
Figure 3.21: Three 50 mN and 8.6 μm radius spherical indentation load-indenter depth of penetration curves of electro-polished tungsten. Pop-ins are present in two of the three.	65
Figure 3.22: A 25 mN load-indenter depth of penetration curve of mechanically-polished tungsten. No pop-ins are present, but given the high elastic modulus of tungsten, neither the 8.6 μm , nor the 3.2 μm could resolve the elastic-plastic transition, which occurs at a depth level too shallow to detect.	66
Figure 3.23: (a). Five successive uniaxial compressive tests of as-drawn high purity polycrystalline titanium rods. (b). A single test pulled from (a) shows the deviation from elastic linearity occurring at a stress of 380 MPa.....	68
Figure 3.24: 750 mN peak load and 500 μm radius spherical indentation load versus indentation depth curve of titanium. Hysteresis is present, and there are no pop-ins.....	69

Figure 3.25: S^3/P versus indentation depth of penetration for a 500 μm radius sapphire sphere indenting a titanium sample. Divergence indicates yielding. ± 10 nm subjective uncertainty boundaries are vertically dashed on either side of the divergence point. The change in S^3/P is more pronounced for the dynamically-sourced continuous stiffness.	70
Figure 4.1: Load-displacement curves for the two pairs of samples. The water-polished BS7.5 is nearly indistinguishable from the oil-polished BS7.5. Conversely, the water polished BS15.7 deforms to a greater depth at the same peak load of 400 mN.	79
Figure 4.2: The elastic modulus plotted as a function of depth for the pairs of samples. At depths below 1500 nm, the water-polished BS15.7 shows much lower elastic modulus than its oil-polished counterpart. A similar but smaller effect is seen for the BS7.5 pair.....	80
Figure 4.3: Berkovich indentation hardness as a function of indenter penetration depth.	82
Figure 4.4: SEM micrographs comparing (a). aqueously-polished and (b). oil-polished surfaces. Porosity appears more prominent and widespread in (a). Some residual polishing marks are visible in (b).	84
Figure 4.5: FTIR absorbance spectra of the four borosilicate glass samples.	85
Figure 4.6: Two segments of the FTIR absorbance spectra focusing on vibrations attributed to the presence of water. Top: asymmetric OH stretching associated more strongly with H_2O Bottom: characteristic bending vibrations of the H_2O molecule	86
Figure 5.1: Load as a function of indentation depth for the three borosilicate glass compositions.	91
Figure 5.2: S^3/P indentation divergence curves for the three borosilicate glass compositions. The dotted vertical lines mark the divergence point for each glass. Colored curves indicate stiffness sourced from continuous dynamic measurement while the black curves indicate the interpolated loading curve stiffness source for each associated composition.....	92
Figure 5.3: FTIR spectra of the three borosilicate compositions	97
Figure 5.4: Raman spectra of the three borosilicate glass compositions	99
Figure 5.5: Size and shape of glass specimens machined for DTDAC testing	102
Figure 5.6: Paris-Edinburgh press apparatus	103
Figure 5.7: The permanent densification amounts measured by float density of fragments of each glass composition after subjection to high-pressure in a DTDAC	105
Figure 5.8: The difference in load as a function of indenter depth from the baseline 0 GPa and 12 GPa is shown for BS15.7 (Top) and BS7.5 (Bottom).	107

Figure 5.9: Elastic modulus as a function of indentation depth from Berkovich nanoindentation comparing the extremes of both compositional and maximum pressure difference.	108
Figure 5.10: Indentation hardness as a function of indentation depth from Berkovich nanoindentation comparing the extremes of both compositional and maximum pressure difference.	109
Figure 5.11: S^3/P as a function of 3.2 μm spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS7.5 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).	110
Figure 5.12: S^3/P as a function of 3.2 μm spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS11.1 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).	111
Figure 5.13: S^3/P as a function of 3.2 μm spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS15.7 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).	112
Figure 5.14: Raman spectra of 0 GPa and 12 GPa pairs of each borosilicate glass composition.	115
Figure 5.15: The progressive state of stress along the central axis of a material indented with a sphere as the applied force increases.	118
Figure 5.16: A snapshot of the state of stress along the central axis at the point of yielding.	119
Figure 5.17: Two purple points mark the yield point determined through spherical indentation of BS11.1 and the point on the x-axis corresponds to the threshold pressure for densification of an ideally pure hydrostatic loading condition. The state of stress during spherical indentation is shown in blue along with two common yield criteria that could be fit as tangent to the indentation stress state.	120

CHAPTER I: INTRODUCTION

Instrumented indentation testing provides the means to efficiently measure many different mechanical properties and characteristics of materials. This is enabled through the richness of information provided by a material's response to indentation contact. Interpreting some mechanical properties traditionally measured by bulk mechanical testing to indentation is often met by challenges related to the intrinsic geometrical constraints imposed by the confinement of material beneath the contact and a free surface outside contact. When probing smaller and smaller scales, the goal of measuring overall bulk material properties with indentation becomes increasingly difficult since the operative mechanisms responsible for bulk continuum behavior have associated length-scales. Nanoindentation leverages this scale dependency, and instead of this necessarily being a burden, it has expanded analysis of mechanical properties and deformation mechanisms to the nanoscale domain.

One mechanical property that is possible to be ascertained from indentation testing is a material's yield stress, the stress state corresponding to the onset of permanent deformation. Obtaining the yield stress is conventionally achieved through uniaxial tests. Empirical correlations between indentation hardness and yield stress have historically been described since the early 20th century.

For readily plastically deforming materials, uniaxial tests are perfectly viable testing options for measuring yield stress, but serious complications arise when testing extremely brittle materials such as glass, namely that brittle materials fracture before any measurable yielding occurs. While important from an engineering perspective, the fracture strength does not carry the same meaning as the yield strength.

A utility of measuring the yield stress in brittle materials is apparent in efforts aimed at modeling the ballistic impact and performance of candidate materials for transparent armor applications [1-3]. Borosilicate glasses comprise one such class of materials [4]. Measuring the yield stress for these materials provides a basis by which structure and property connections related to the deformation behavior may be formed. It is to this end that the central motivation

guiding this work is to use indentation to estimate the yield stress of three borosilicate glasses, distinguished chiefly by their respective molar ratio concentrations of silicate to borate.

In order to accomplish this, a new method by which the yield stress is found is developed in Chapter III, but first a background overview of the subject matter is presented in Chapter II. The necessity of the development of a new indentation methodology is fostered by the paucity of techniques applicable to brittle materials. The applicability of this new method, nevertheless, will be shown to be valid for brittle and non-brittle materials alike, provided that the assumptions underlying the method are reasonably met. The value of using spherical indentation in the pursuit of identifying the yield stress as opposed to sharp indenters such as cones, three-sided pyramidal Berkovich, or four-sided pyramidal Vickers indenters is demonstrated. Experimentally producing just a number that theoretically should be the yield stress by itself is insufficient to comprehensively substantiate that the number is indeed the yield stress proper. Therefore, to test the veracity of the output of method, an independent measurement of the yield stress was achieved with uniaxial compression testing of titanium.

Practical issues of surface preparation directly related to the central borosilicate glass system investigated are addressed in Chapter IV. The effect of water interaction during the process of planarization (grinding and polishing) on the alteration of near-surface mechanical properties measured using nanoindentation and bonding structure is studied in particular. The relevance of this inquiry into surface processing is that any alteration of the surface could adversely influence characterization of bulk mechanical properties like the yield stress since the alteration would not be representative of the structure or properties of the bulk sample. Structural bonding information is elucidated using Fourier Transform Infrared Spectroscopy (FTIR).

With a novel method to estimate the yield stress using indentation fully developed and described along with the lessons learned from surface preparation implemented, finally, the yielding characteristics of the three borosilicate glass compositions and the tacit connection to

the structure is explored in Chapter V. In addition to estimating the yield stress of the three glasses at standard temperature and atmospheric pressure, the effect of nominally high hydrostatic pressure (~12 GPa) on the yield properties of recovered samples is evaluated.

Aiding in the analysis of any structural basis for yielding differences between the glasses are vibrational spectroscopic techniques (infrared and Raman). The comparable place yield stress holds with respect to indentation hardness, elastic moduli, and density is also examined.

CHAPTER II: OVERVIEW OF BOROSILICATE GLASS STRUCTURE AND INDENTATION DEFORMATION CHARACTERISTICS

What exactly is the structure of glass and specifically the structure of borosilicate glass?

Glass in the broadest sense is an amorphous solid. It has no long-range periodicity as seen in crystalline matter. Glasses are most often formed by quenching from a temperature above their melting points to a temperature where there is a non-equilibrium rate of dynamic structural rearrangement. The rearrangement progresses so slowly that the molecules have insufficient time to form an ordered crystalline structure. The structure of the melt becomes frozen-in [5]. Glasses lack the periodic long-range order of crystalline systems. Direct experimental evidence for this fact comes from neutron and X-Ray diffraction, whereas for crystals, conditions for constructive interference appear as sharp peaks associated with the spacing between coordinated periodicity of lattice plane spacing. In amorphous systems, sharp peaks are nonexistent because there is no periodic elementary cell. Even though there is no evidence for long range order as seen in crystals, order is present at smaller scales [5]. A pair density correlation distribution function can be generated that represents the probability of finding another atom as a function of a distance from a central atom. Peaks correlated with the distance between successive neighbors are present, but only for the first few neighbors. The farther away from the central atom, there is less regularity in the position of neighbors due to the effect of compounding successive misplacement (relative to a perfectly ordered system) in three-dimensional space.

Glass Structural Characteristics

Silicate

Intermediate range order is present in inorganic glasses that are comprised of basic molecular units such as corner-sharing tetrahedral $\{\text{SiO}_4\}$. Deviation from the idealized angle between Si-O-Si and dihedral angle rotation disorder the connectivity of the system. The longest range order observed in the topology glasses is the statistics of ring sizes. The variation in ring sizes directly results from the variable bond and dihedral angles [7]. This continuous random

network theory of glass structure was introduced by Zachariasen in 1932 [8]. In its original form, it is only applicable when the network is not modified by a cation that disrupts the connectivity of the oxide network. Advancements in theoretical descriptions have since been made that incorporate differently-sized network forming and network modifying polyhedra within a glass [9]. The addition of too many alkali or alkaline-earth modifier ions ultimately results depolymerization of the network through the generation of non-bridging oxygens [10][11].

Borate

Vitreous B_2O_3 and borate glasses have been studied extensively by Raman spectroscopy, neutron scattering, and nuclear magnetic resonance spectroscopy [12]. These studies reveal that the B_2O_3 structure largely consists of boroxol rings constructed from corner-shared $\{BO_3\}$ triangles [13]. The network connectivity of the rings is mediated by non ring-member $\{BO_3\}$ triangular structural units. In contrast to silicate glasses, when modifier ions are initially added to borate glass, a non-bridging oxygen is not formed. Instead, $\{BO_3\}$ groups are converted to tetrahedrally-coordinated $\{BO_4\}$ [14][15]. However, there is a saturation point to the conversion of $\{BO_3\}$ to $\{BO_4\}$. When the ratio of alkali oxide to B_2O_3 reaches 0.5, an inverse reaction takes place ($\{BO_4\}$ concentration decreases corresponding to formation of $\{BO_3\}$ with non-bridging oxygens) [16].

Borosilicate

The structure of borosilicate glasses in this present work has a composition containing SiO_2 - B_2O_3 - Na_2O - Al_2O_3 in decreasing molar concentration. The composition of each glass is shown in Table 2.1. It would make intuitive sense if the structure would be a simple combination of the B_2O_3 and SiO_2 glasses. In network forming glass, however, its inherent random nature renders simple qualitative descriptions difficult, especially when network modifiers are added to the composition. The structure of borosilicate glass varies depending on the coordination of the

Table 2.1: Molar Composition of Each Studied Glass

Glass Name	SiO₂	B₂O₃	Na₂O	Al₂O₃	K₂O	BaO
BS7.5	87.6%	7.5%	3.3%	1.2%	0.3%	0.1%
BS11.1 (Borofloat®)	83.7%	11.1%	3.4%	1.5%	0.4%	0.0%
BS15.7	79.3%	15.7%	3.4%	1.3%	0.3%	0.0%

boron and the character of non-bridging oxygens, the latter of which is related to the ratio of alkali oxide and silicon oxide to B_2O_3 [17]. As network modifiers, such as Na_2O , are incorporated into the glass, density, the glass transition temperature, hardness, and network connectivity increase to a maximum and then decrease thereafter. A reversal occurs when the ratio between Na_2O and B_2O_3 exceeds 0.5, which is attributable to the establishment of $\{BO_3\}$ structural units with non-bridging oxygens. This transformation progressively breaks the interconnections of the glass network. In low concentrations, alkali oxides have the effect of transforming $\{BO_3\}$ to $\{BO_4\}$ without the introduction of non-bridging oxygens [18]. There is an internal competition between the silicate tetrahedra and trigonal borate groups as to whether a non-bridging oxygen will form on either in the presence of an alkali oxide modifier. Initially, the borate usually wins the bond to the alkali oxide, and this bond preference has been observed to exacerbate phase separation [19]. The introduction of Al_2O_3 to the borosilicate glass composition decreases the concentration of $\{BO_4\}$ units. Adding alumina inhibits segregation and phase separation due to network connectivity competition between the other network forming cations in the glass [20]. SiO_2 is integrated into the structure through fully linked $\{SiO_4\}$ tetrahedra. Decreases in network connectivity are related to corresponding decreases in hardness [21].

Composition of Materials

The glass compositions studied in this work are predominantly silicate with small additions of Na_2O and Al_2O_3 . Three borosilicate glass compositions were tested and are designated as BS7.5, BS11.1 (Borofloat®), and BS15.7. The compositions are labeled BSX where the label X refers to the molar percentage of borate. The molar compositions and molar ratios K (SiO_2/B_2O_3) and R (Na_2O/B_2O_3) for the glasses are listed in Table 2.2. The selection of

Table 2.2: Compositional Molar Ratios and Poisson Ratio from Resonant Ultrasonic Spectroscopy

Glass Name	R ($\text{Na}_2\text{O}/\text{B}_2\text{O}_3$)	K ($\text{SiO}_2/\text{B}_2\text{O}_3$)	R/K	ν
BS7.5	0.45	11.7	0.038	0.17
BS11.1	0.31	7.55	0.041	0.18
BS15.7	0.21	5.04	0.042	0.205

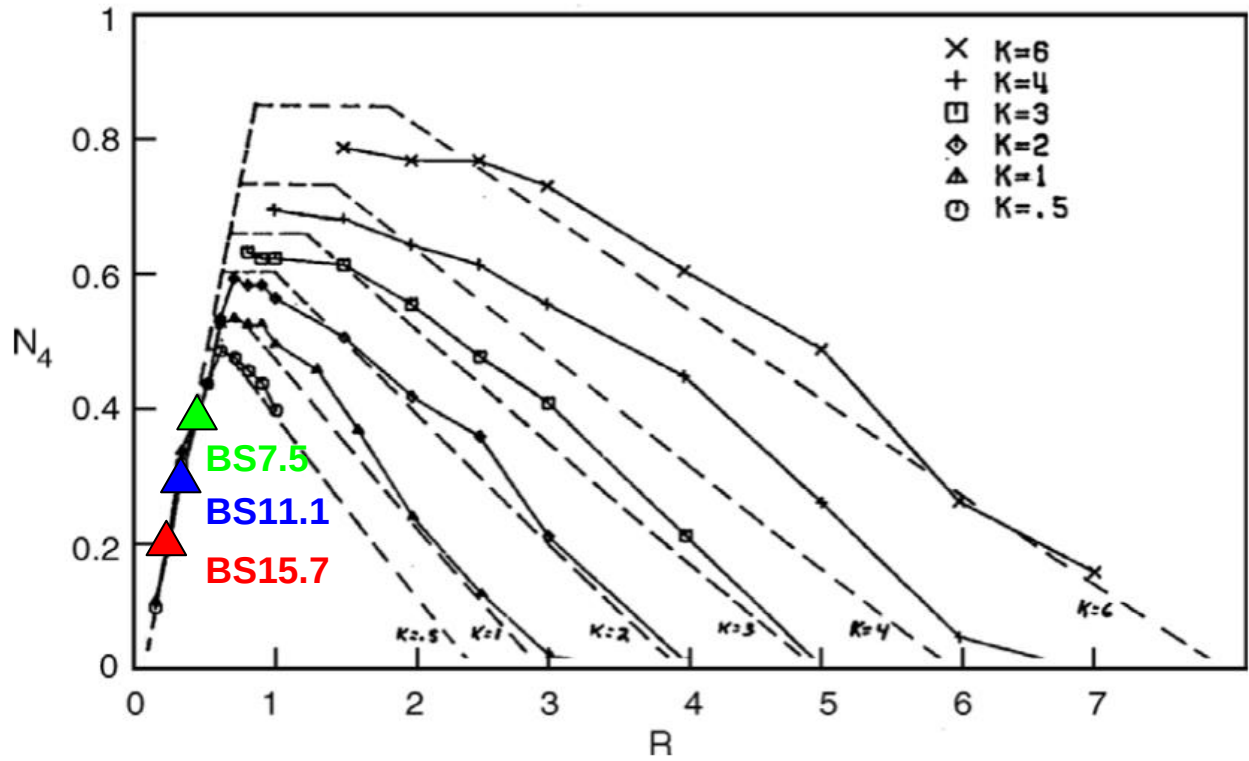


Figure 2.1: The K and R ratios of each of the three glass compositions allow for their placement on this established structural model of $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O}$ glass from Yun Bray and Dell [22][23] establishing N_4 , the decimal fraction of boron that is tetrahedrally coordinated.

these compositions was motivated by investigating a possible relationship between deformation behavior and the composition. The three glass compositions are placed in Fig. 2.1 according to the Yun, Bray, and Dell model [22][23] to show differences in the fractions of tetrahedrally coordinated borate groups.

The choice of the glass composition scheme to analyze was developed around the commercial borosilicate glass, Borofloat®, produced by Schott Glass. Two additional compositions were provided by the US Army Research Laboratory and are distinguished from Borofloat® through alteration of the SiO_2 / B_2O_3 ratio: one glass having higher relative molar borate concentration (15.7 mol %), the other having lower (7.5 mol %). The borate molar ratio for Borofloat® itself is 11.1 mol %. This range of compositions facilitates study of the relative contribution each sub-network (SiO_2 and B_2O_3) has on the yielding characteristics. A ternary composition diagram for the glass system is shown in Fig. 2.2.

Mechanical Deformation Modes of Glass

Elastic deformation

At low stresses, the deformation of glass lies within a classical linear elastic regime. Bonds are stretched but then recover back to their original lengths upon unloading, and this gives rise to linear elastic properties. In an ideal glass, the bulk network acts as an isotropic solid. Elastic moduli can be directly ascertained from resonant ultrasonic spectroscopy. The story at the atomic level is much different with regard to the extent of the basic structural differences between amorphous and crystalline solids. In the former, the local strain tensor varies even at small stresses for each atom in the glass [24]. Displacements on the atomic scale in glass are not congruently synchronized. For bulk continuum mechanics, these local effects are averaged out. Elastic moduli are dependent upon: interatomic bonding energy, coordination, polymerization degree, atomic packing density, and molecular organization [25][26].

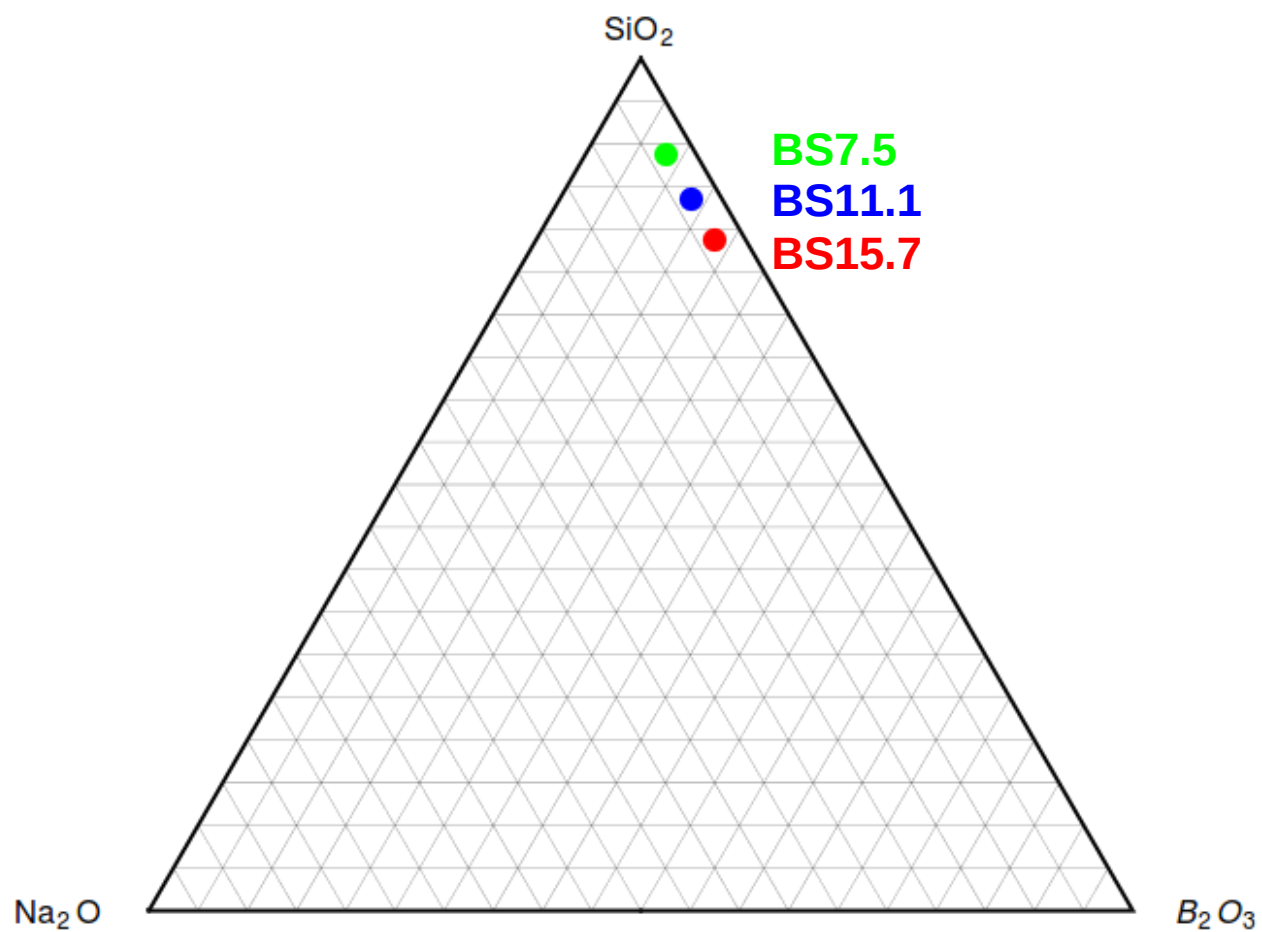


Figure 2.2: Composition triangle of the three glasses studied in depth in this work absent the small (~ 1 mol%) alumina contribution.

Densification

Confined compression testing has shown that some glasses will undergo a structural rearrangement at high pressure [27]. Unlike elastic deformation, this volumetric strain accommodating structural rearrangement can be permanent in the sense of the structure not returning to its original configuration upon unloading [28]. The amount of densification is defined by the ratio of the change in volume to the original volume. In silicate and borate glasses, the application of a critical hydrostatic pressure transforms the internal structure, and the material is compressed into a smaller volume, thereby increasing the density [29]. The degree to which glasses densify has been correlated to Poisson's ratio and the amount of free volume. [25] Fused silica has been observed to densify up to 20% [29]. Lower Poisson ratios carry an implication of having less network connectivity and therefore a decreased hindrance for structural rearrangement. The same can be said for the free volume. Glasses with more free volume have been shown to densify more than glasses with a lack of free space like metallic glasses. The nature of the structural rearrangement does not manifest itself in the form of shortening of bond lengths. Instead, the principal process at work for fused silica is the rotation and bending of inter-tetrahedral bond angles [30]. Raman spectroscopy studies have indicated that the SiO_2 sub-network allows for the densification of borosilicate glasses with compositions related to the ones studied in this work [31][32]. Densification is realized by an increasing amount of smaller silicate rings (three and four members) and a corresponding decrease in the amount of larger silicate rings (five and six members). There is also an observed decrease of the Si-O-Si bond angle. The connectivity between the silicate and borate sub-networks increases continuously as the Na_2O and B_2O_3 concentrations increase. The ability of the borosilicate glass with increasing concentration of network modifiers to densify is hypothesized to decrease due to the linkage and ring-forming of $\{\text{BO}_4\}$ and $\{\text{SiO}_4\}$ tetrahedra in this case [33]. Vitreous B_2O_3 shows only a small fraction of the densification observed for glassy SiO_2 [29][34]. This suggests that the dominating deformation process in the borate glasses would be more

shear driven rather than densification driven. Densification of B_2O_3 containing glasses has been described by the breakage of three-membered boroxol rings during loading and the conversion of $\{BO_3\}$ units into temporary $\{BO_4\}$ groups [35]. Though $\{BO_4\}$ groups are reverted to $\{BO_3\}$ after unloading, only a small fraction of the previously existing boroxol rings are restored. Permanent densification is achieved as a consequence of the reduced free volume inside the glass network stemming from ring termination. Densification is a complicated process that can involve numerous variations of structural rearrangement. Another distinct aspect of the densification of inorganic glasses is that it is thermally reversible [36-38]. Annealing a densified glass sample causes it to return to its pre-densified volume.

Plastic deformation

When early pressure experiments were conducted on vitreous silica, an apparent difference in the critical stress necessary to induce densification became evident [29][39]. The source of this has been ascribed to shear. Across different experimenters, the pressurizing media and cells relayed differing amounts of shear in relation to hydrostatic stress. It was concluded that shear lowered the threshold for densification. Fig. 2.3 from [29] plots densification versus pressure and shows what effect increasing the amount of shear has on the densification threshold. Shear flow, deformation not attributable to densification, does still occur in SiO_2 glass [40]. However, the observed shearing flow has been limited to a nanometer scale, and deformation on a larger scale has been accompanied by cracking [41]. Additional evidence for plasticity comes from curved shavings from scratching [39], pileup and crack systems resembling slip lines during indentation [41], and micropillar tests [42]. The exact atomic mechanism that causes this shearing behavior still is not fully understood, but it does lend credence to a complex competition and cooperation of shear and densifying processes [43]. Irreversible shear flow mechanisms for the borosilicate glass compositions in this work must be considered different from the ones found in soda-lime silicate glasses, which are suspected to

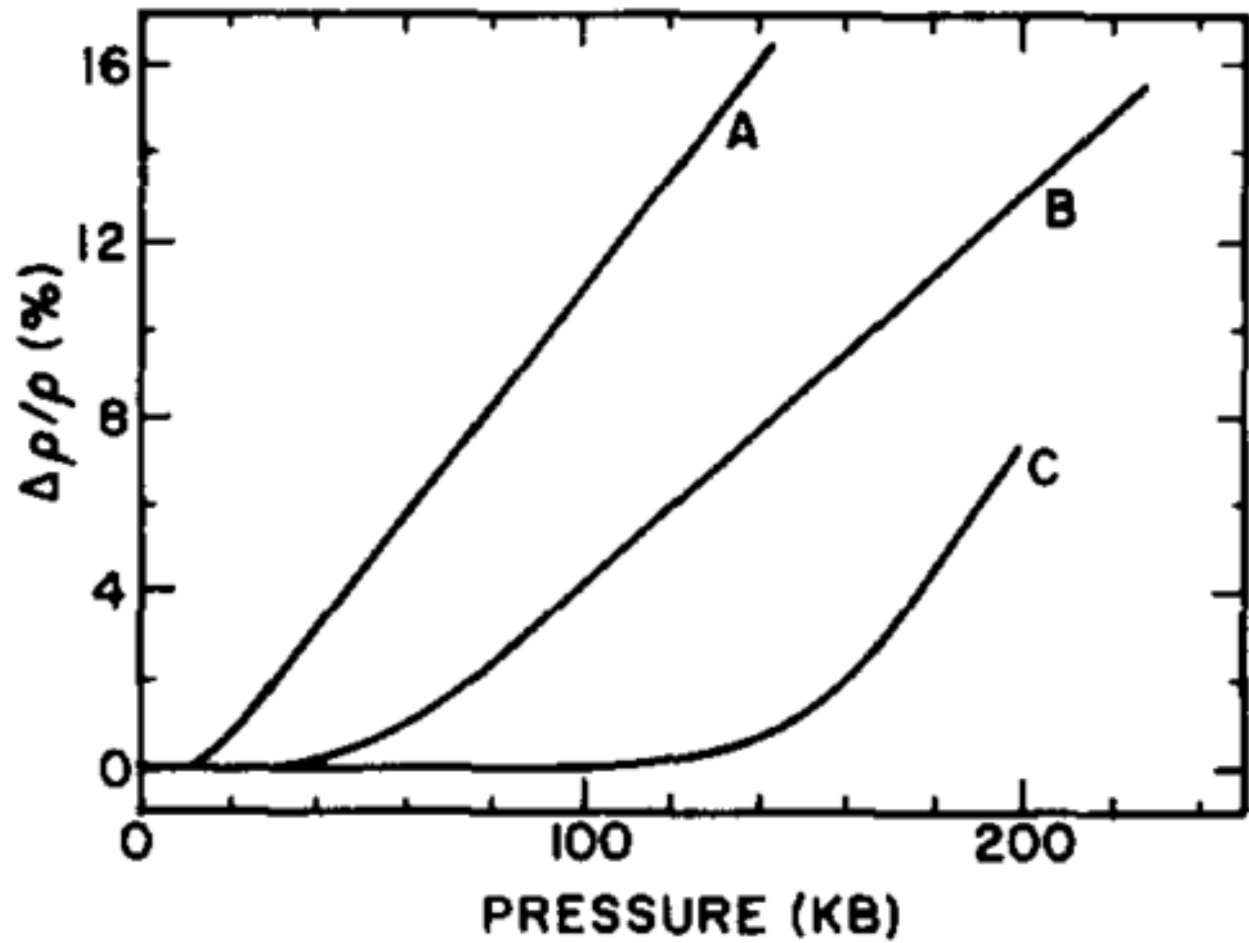


Figure 2.3: Permanent densification versus pressure curves of fused silica compressed in three different media that transmitted different amounts of shear from [29]. $A > B > C$ in terms of the magnitude of the shear. Higher shear components depress the threshold pressure necessary for densification to proceed. 100kb = 10GPa

deform through shear flow of the more weakly bonded network modifiers (Ca, Mg, Na) regions [44]. Plastic flow of glass under pressure currently lacks a detailed understanding of the dynamics of atomic structural changes.

Theoretical Underpinnings of Indentation of Glass

Historical development of indentation theory

Indentation is the keystone of this research as it pertains to the investigation of the yielding properties of borosilicate glasses, which are candidates for transparent armor applications. Historically, indentation began as a quick, simple, and non-destructive test of a material's resistance to deformation. The theory underscoring indentation was advanced seminally by Hertz's work with lenses, which was cleverly applied to the elastic contact problem involving spheres [45]. In the case of an indenting sphere, the stress field which develops in a perfectly elastic material subject to indentation could be described analytically as a function of indenter radius, applied load, and depth of indenter penetration acting on an elastic half-space. This description of the elastic stress field was later extended to any axisymmetric and smooth tip profile by Sneddon [46]. Contact theory doesn't just end at descriptions of elasticity. Permanent impressions can form from indentation, too. Tabor made important contributions incorporating the theory of plasticity and hardness into the indentation process. Indentation in metals was separated into the characteristic regions of elastic loading, elastic-plastic loading, plastic loading, and finally elastic unloading. The mean contact pressure of a perfectly plastic material was shown to be related to the yield stress of the material under uniaxial compression by a constraint proportionality factor approximately equal to three [47].

Underestimations of the mean pressure when using the constraint factor of three with materials that had a large contribution of elasticity to indentation strains led to Johnson, building off of the work of Hill [48], who modeled the plastic portion indentation as an expanding spherical cavity driven by an internal pressure, to develop a model for contact plasticity that

could account for both the volume of material displaced by indenter and from elastic expansion [49].

Indentation deformation of normal and anomalous glass

Glass usually fractures in response to conventional mechanical testing methods before any deformation mode can manifest itself. In order to inhibit fracture during testing, tensile stresses must be minimized. Since an indentation is comprised of mainly compressive and shearing stresses with relatively low amounts of tensile stress components, it is well-suited for the study of brittle materials. The utility of indentation to elucidate mechanical behavior and its consequent link to the structure of glass has been well-documented [50-52]. Load, hardness, and elastic modulus as a function of contact depth can be generated systematically with instrumented nanoindentation [53].

Certain glasses have been branded with the term “normal” since they behave in ways typified by most crystalline solids. Other glasses, fused silica for example, show anomalous mechanical behavior such as compressibility and densification initially increasing upon an increase in pressure. The difference in the activity of different deformation mechanisms (greater volume compaction for anomalous glass than shearing and vice versa for normal glass) explains much of the anomalous behavior of the mechanical properties. Anomalous glasses were found to be more likely to form ring-type cracks as opposed to classical median crack systems [54].

Stresses that develop beneath the contact with the surface of smooth, axisymmetric indenters are well defined. The stress states have hydrostatic and shear components on the order of the high pressures can be achieved with diamond anvil cells (~12 GPa). This is especially important because it demonstrates that indentation can reach the same hydrostatic pressures necessary to cause densification [50] and, at the same time, apply deviatoric stresses central to shear flow [39][41]. However, such a sharp demarcation of separate roles hydrostatic

and shear stress play may not be an accurate interpretation of the joint atomic scale interactions within currently formulated constitutive relations.

Blunter indenter tips, having a larger component of hydrostatic stress, have been shown to preferentially promote densification [55]. The physical impressions that are formed through indentation along with accompanying loading and contact area information provide a wealth of knowledge regarding the physical processes at play during deformation, such as the interplay between plastic flow and densification [56].

Even though glasses are macroscopically brittle, nanoindentation often results in the formation of permanent impressions in glasses. Unlike periodically ordered crystalline structures, plastic flow is not accommodated by the nucleation and motion of dislocations. If not dislocations, there still must be some mechanism to allow for glass to deform in a plastic manner. The most that can be attested regarding this theoretical dilemma is understanding that shearing deformation occurs along lines of localized atomic scale rearrangement, irreversibly affecting local network topology in the sense of creating the impossibility of a local atomic configuration to spontaneously recover to its pre-deformed position or bonding arrangement. Detailed explanations of such changes are still open questions in the field.

Inducing indentation deformation in glass has allowed numerous investigators to probe constitutive relations and internal structural changes [59-69]. Small-scale micro-pillar compression has aided in this area too [45]. Raman spectroscopy of indents has shown possible structural changes associated with densification as a result of indentation. A shortcoming of that approach is the intervening factor of residual stresses, whose Raman shift signature cannot be simply deconvoluted. Since the initial structure of glass prior to densification can be thermally recoverable, a measure of the degree of densification that is present after an indent has been formed can be deduced by measuring the volume of an indent before and after thermal annealing treatment [58]. A higher degree densification would correlate to an increased amount of volume recovery. Constitutive laws describing the indentation response of glasses

have been developed and calibrated with experimental extremes (pure shear [42] and hydrostatic pressure [59] derived from real [40] and molecular dynamics simulation [62]), but thus far theoretically, the gulf between atomic scale and bulk processes has not been bridged.

CHAPTER III: EXPLICATION OF A NOVEL TECHNIQUE TO ESTIMATE YIELD STRESS USING SPHERICAL INDENTATION

Elements of this chapter have been published in Hackett, B. L., Andrew A. Wereszczak, and G. M. Pharr. "Evaluation of New Technique to Estimate Yield Stress in Brittle Materials Via Spherical Indentation Testing." *Proceeding of the 42nd International Conference on Advanced Ceramics and Composites: Ceramic Engineering and Science Proceedings* Volume 39, Issue 2. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2019.

Background and Motivation for Developing New Method

To yield generally means to give way. In a material sense, this simple concept of giving way to an applied force has engendered entire fields of study. Yielding occurs at a critical stress state in which a material can no longer accommodate purely elastic deformation and whereby the shape of a material is permanently deformed. The stress at which a material permanently deforms is an important material property that harbors tremendous value in the process of assessing the suitability and predicting the mechanical performance of materials for diverse applications. Unlike hardness, yield stress is a mechanical property distinct from geometric dependency.

For brittle materials, the yielding properties are often neglected and are instead supplanted by fracture characteristics and statistics. One practical reason for this neglect is that conventional bulk testing methods to find the yield stress, such as uniaxial compression tests, are nonviable when applied to brittle materials due to fracture often preceding detectable yielding. By reducing the deformation zone to a small constrained volume, instrumented indentation testing allows for analysis of small-scale permanent deformation unaccompanied by catastrophic fracture failure.

The usage of an applicable yield criterion combined with knowledge of the stress state that develops between the contact of an indenter of a given geometry and the material surface enables relation to conventional uniaxial stress testing configurations. The indentation response and the bulk mechanical response can then be linked.

One main objective of this work is to evaluate the onset of non-recoverable deformation and use the detection of that onset to estimate the yield stress of a trio of borosilicate glasses. This is prompted in part by the inclusion of deformation properties in constitutive equations used in modeling the mechanical behavior of brittle materials. For example, models of the ballistic impact performance of transparent armor have relied on measures of the yield strength [1-3]. The impetus for the development of a new method using spherical indentation to establish confident estimates of the yield stress in brittle materials stems from shortcomings of prior attempts.

Rationale for using spherical indentation

Identification of the mean contact pressure at which the material first yields during a spherical indentation test was originally suggested by Hertz to be the definition of hardness [68]. However, in practice, the determination of this point has been experimentally difficult due to the very gradual deviation from perfect elasticity of a material's load-displacement curve. As a spherical indenter is pressed into a glass surface, the material first accommodates the applied pressure by means of an elastic response. Next, stresses reach a level where irreversible volume-conserving plastic-like flow initiates. Possibly simultaneously, non-volume-conserving densification of the structure may also commence in response to the increasing stress. Both of these mechanisms can result in the emergence of a residual hardness impression [60].

Comparison to extant methodologies

Despite this limitation, using a spherical indenter to find the critical yielding point and accompanying stresses at which the formation of a permanent impression occurs has been pursued using optical techniques [69-71], plotting indentation stress versus indentation strain [71-73], and extrapolating the permanent impression depth as a function of peak load [71]. The experimental error of the latter two techniques to establish the yield stress of a soda-lime glass is large (± 1 GPa). Furthermore, the true accuracy of the yield stress reported using those

techniques is unknown since no corroboration with yield stress derived from conventional techniques was attempted. Another technique involving the ratio of contact depth to total depth, which should be equal to 0.5 if within an elastic regime, has also been tried with limited success on an aluminum alloy [74]. Overall, the common deficiency present for the described instrumental techniques involve lack of precision coming from experimental difficulty in accounting for the gradual transition of the deformation mode.

Absent from mention so far are the numerous attempts to use finite element models to fit experimental data and calculate material properties [75-79]. Many of these reverse analysis approaches suffer from a departure from physical grounding needing multitudes of empirical fitting parameters. There are also issues with lack of uniqueness of solutions and narrow range of applicability [80].

Sharp indenters have also been used to approach the problem of the determination of yield stress from indentation [81-83]. The main deficiency of using sharp indenters with brittle materials is that a plastic indentation response occurs immediately upon loading requiring reliance on modeling yield criteria and constitutive equations that had been originally developed to describe plasticity in metals. Those core relations do not account for non-volume-conserving permanent deformation.

Advantages of newly devised method

The new technique developed in this work to overcome the limitations of previous efforts bears no need for multiple experiments beyond statistical concerns and does not rely upon finite element methods. The main theoretical advantage of this new technique is its foundation in the fundamental measurements obtained during instrumented indentation: the displacement of the indenter into the sample material and the associated force applied to the indenter. There is physical meaning to the parameter derived from those core measurements. Both of these measurements are determined with high precision in modern instrumented indenters. The main

practical advantage of the technique is that a valid value for the yield stress can in principle be obtained from a single test.

Theoretical Description of the Methodology

In order to determine the stress state at yielding the point of onset of permanent deformation itself must first be detected. Permanent deformation in this case refers to deformation which is not recovered upon unloading. Detection of a crossover point between recoverable (elastic) and non-recoverable deformation during the course of a spherical indentation is achieved through sensing the formation of a permanent impression. A representative load-displacement curve resulting from spherical indentation of a brittle material is shown in Fig. 3.1. The dashed line is the tangent line to the unloading curve at the maximum load. The slope of this line is the contact stiffness at the point of first unloading. Following Joslin and Oliver [84], who in part demonstrated that the elastic contact stiffness (S) squared divided by the load (P) results in a value that is constant with depth for geometrically self-similar indenters, it can be shown that for spherical indenters the analogous depth-independent elastic parameter is S^3/P . The usefulness of this approach is that the contact stiffness is directly linked by differentiation to the applied load and displacement, which are the fundamental quantities measurable to a high degree of precision and accuracy by modern instrumented indenters. The S^3/P parameter can be obtained through two independent sources: stiffness interpolated from the instantaneous slope along the loading-displacement curve and the continuously measured dynamic unloading stiffness. Continuous stiffness measurements are made using the dynamic unloading characteristics of small oscillating load and unload cycles superimposed on the general loading curve [85]. Interpolation of the loading curve and continuous stiffness measurement become increasingly intractable at low depths ($<50\text{nm}$) because of higher levels of noise.

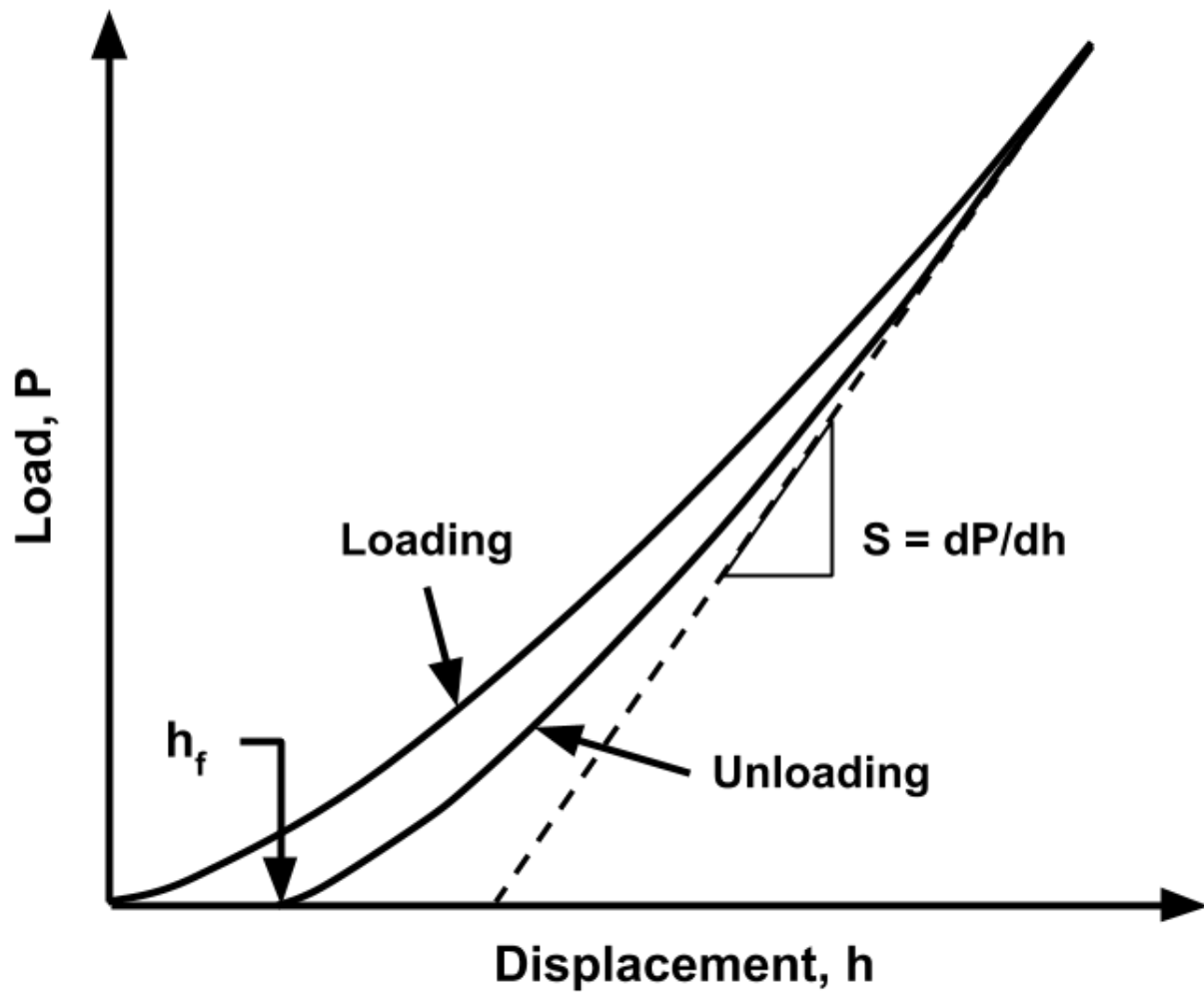


Figure 3.1: Illustrative load-displacement curve of a material exhibiting loading-unloading hysteresis from non-recovered deformation and corresponding residual depth, h_f . Stiffness is taken as the instantaneous slope of the unloading curve at the peak load.

Contact stiffness (S) from dynamic response is continuously calculated using Equation (3.1) below. F_0 is the amplitude of the force signal, z_0 is the amplitude of the displacement signal, ϕ is the phase angle between the force and displacement signals, K_i is spring stiffness, m is the mass of the indenter, ω is the frequency of oscillation, and K_f is the frame stiffness.

$$S = \left[\frac{1}{\frac{F_0}{z_0} \cos \phi - (K_i - m\omega^2)} - \frac{1}{K_f} \right]^{-1} \quad (3.1)$$

The S^3/P parameter is a function of only the reduced Young's modulus (E^*), and the relative radius of curvature (R) of the spherical indenter (R_1) and surface (R_2). These parameters are defined by:

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad (3.2)$$

$$R = \left(\frac{1}{R_1} - \frac{1}{R_2} \right)^{-1} \quad (3.3)$$

where E_1 and ν_1 are the Young's modulus and Poisson's ratio for the indenter, respectively, and E_2 and ν_2 are the same quantities for the specimen. Note that a change in curvature of the surface attributable to the formation of a permanent impression serves to change the effective radius of the indenter, and thus S^3/P will change accordingly.

Beginning with the Hertzian expression for load as a function of penetration depth for elastic contact involving a sphere (approximated by a paraboloid) and a flat surface ($R_2 = \infty$) we have that

$$P = \frac{4}{3}E^*\sqrt{R}(h - h_f)^{3/2} \quad (3.4)$$

and differentiating Equation (3.4) with respect to elastic displacement relative to the undeformed surface, $h - h_f$, results in the stiffness

$$S = \frac{dP}{dh} = 2E^*\sqrt{R}(h - h_f)^{1/2} \quad (3.5)$$

Here, h is the total indenter displacement relative to the initial undeformed surface, and h_f is the permanent depth of penetration after complete unloading. By cubing Equation (3.5) and dividing it by Equation (3.4), the depth dependency cancels out yielding the parameter

$$\frac{S^3}{P} = 6E^{*2}R \quad (3.6)$$

The significance of Equation (3.6) will soon become clear. If a material deforms solely by elastic processes during spherical indentation, the loading-derived stiffness and unloading-derived stiffness will be equivalent. This is because when a material's mechanical behavior is perfectly represented by elasticity, the loading and unloading curves are identical with no hysteresis. Conversely, if permanent deformation occurs, a change to surface curvature results, and this in turn increases R in Equation (3.6). At the same time, the loading-derived stiffness decreases because loading now involves accommodation of deformation by elastic and non-elastic means. The material can no longer support the imposed stress by purely elastic deformation processes. Just as in a uniaxial tensile test, when the elastic limit is met, the stress-

strain curve begins to negatively deviate from linear elastic proportionality. A schematic of this process is shown in Fig. 3.2 with the divergence point defined as the onset of yielding.

The critical mean contact pressure corresponding with the initiation of yielding behavior is not the same as the macroscopic yield strength found through a uniaxial loading condition. In order to relate the two, a constitutive relation and accompanying yield criterion must be applied. One of the simplest yield criteria is that of Tresca, and is also known as the maximum shear stress criterion. It states that yielding occurs when the maximum shear stress reaches a critical value and has wide-ranging applicability to homogeneous isotropic solids in which yielding has a plastic component. Owing to the fact that the stress state beneath a spherical indenter during elastic deformation is well described analytically, the depth where the shear stress is at a maximum is known, and thus a conversion between the contact pressure and the uniaxially derived yield strength of a material can be made. The veracity of the estimation of yield strength is dependent upon how closely the yield surface specified by yield criteria agrees with experimental results of the stress states present at the point of yielding across different loading conditions. Choosing or developing yielding criteria that contain components carrying physical significance to characteristics of experimentally observed mechanical responses is paramount in achieving accurate quantitative descriptions and predictors of mechanical behavior. A schematic of the contact is shown in Fig. 3.3. The equivalent radial (σ_r) and circumferential (σ_θ) principal stresses along the z-axis are given by [49]:

$$\frac{\sigma_r}{p_0} = \frac{\sigma_\theta}{p_0} = -(1 + \nu)(1 - (z/a) \tan^{-1}[a/z]) + \frac{1}{2}(1 + z^2/a^2)^{-1} \quad (3.6)$$

where p_0 is the maximum pressure, ν is Poisson's ratio, z is the vertical distance below the surface, and a is the contact radius.

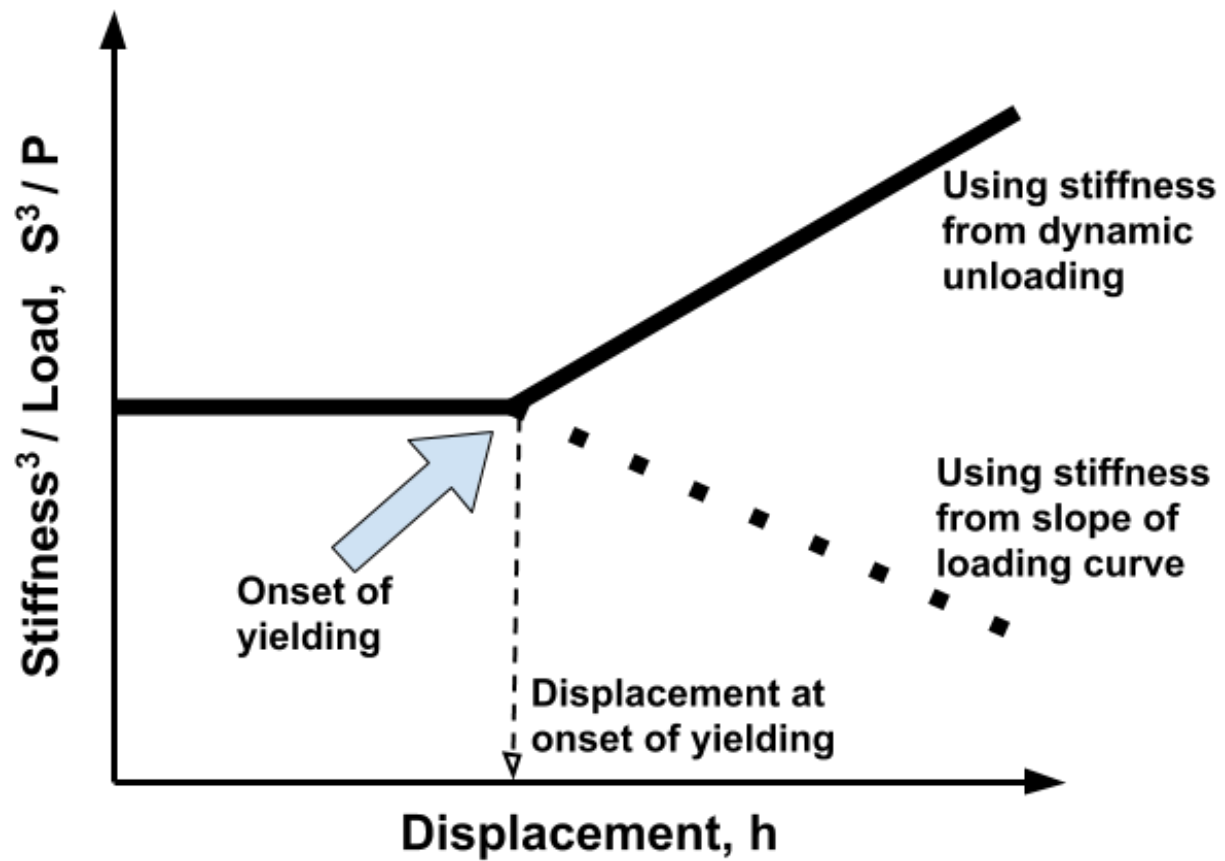


Figure 3.2: Schematic representation of S^3/P as a function of the displacement of an indenter into a surface. The effect of two different approaches to calculating the stiffness in S^3/P is shown. The dynamic unloading stiffness (solid line) is found by continuous stiffness measurement, while the loading stiffness (dotted line) is found using the slope of the loading curve. The two lines overlap in the perfectly elastic regime. The onset of permanent deformation is indicated when the two approaches to calculating S^3/P diverge.

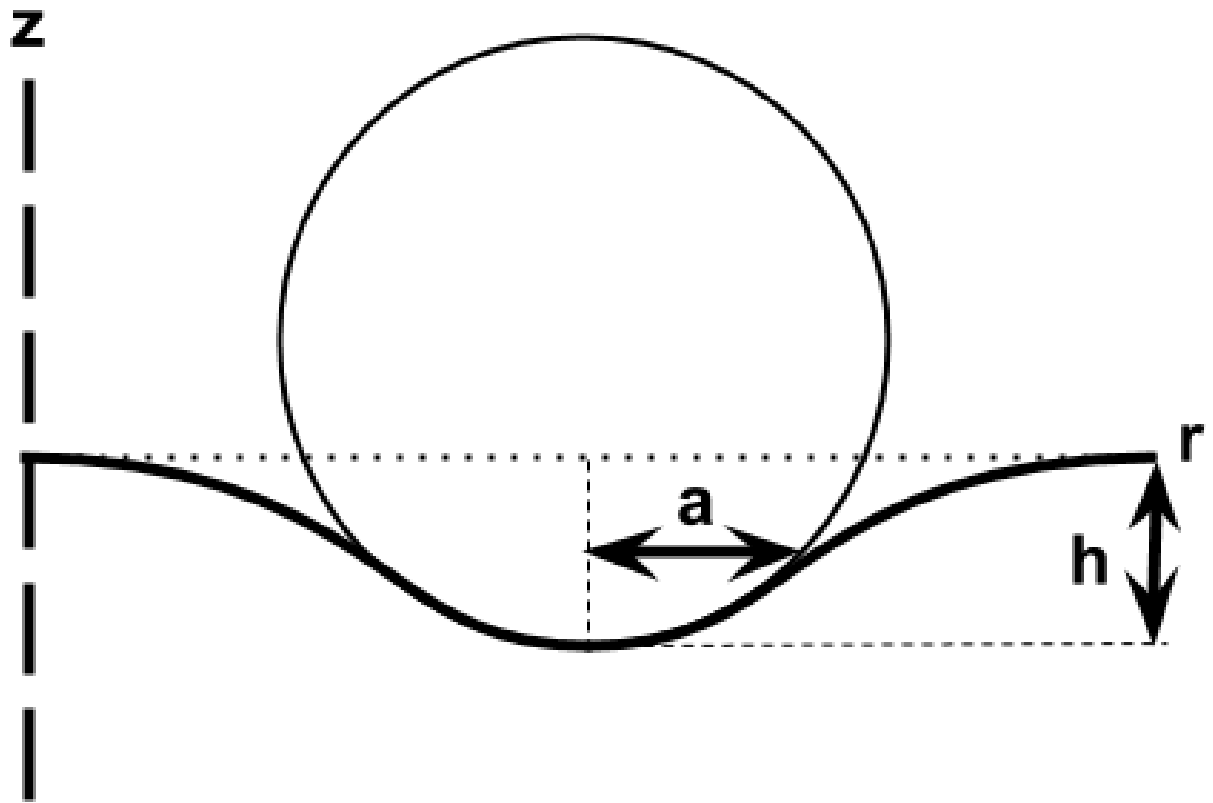


Figure 3.3: Schematic depiction of rigid spherical elastic contact with a flat surface

The maximum principal stress in the z direction is given by [49]:

$$\frac{\sigma_z}{p_0} = -(1 + z^2/a^2)^{-1} \quad (3.7)$$

Letting $\tau_{\max}$ be the maximum shear stress and σ_y the uniaxial yield strength, it follows that

$$\tau_{\max} = \frac{1}{2} |\sigma_z - \sigma_r| \quad (3.8a)$$

$$\tau = \frac{\sigma_y}{2} \quad (3.8b)$$

$$p_0 = \frac{3}{2} p_m \quad (3.9a)$$

$$p_m = \frac{P}{\pi R h} \quad (3.9b)$$

where p_m is the averaged or mean pressure in the contact interface. Substituting Equations (3.6), (3.7), and (3.9) into Equation (3.8a) and noting the necessity of equivalency of the maximum shear stress criterion ($3.8a = 3.8b$) at the onset of yielding permits the estimation of the yield stress using the corresponding values of v , P , h , R , and depth of the maximum shear stress in terms of z/a .

$$\sigma_y \approx 1.016 p_m \quad \text{for } v = 0.18 \quad (3.10)$$

The shear stress field intensity that develops underneath the indenter during contact according to Equation (3.8a) is shown in Fig. 3.4. Note that the maximum shear stress occurs at some depth z/a beneath the surface. The coincident hydrostatic stress field is shown in Fig. 3.5. The highest stress concentration occurs at the surface.

Practical Considerations Necessary for Accurate Determination of Yield Stress

Selection of indenter radii size

It must be understood that practical analysis of elastic to plastic deformation transition depends upon the size of an indenter and the elastic properties of the target material. Consideration of both of those two parameters is needed in order to generate the necessary stresses to initiate permanent deformation. The transition from elastic to plastic deformation must be traversed during the course of load application in order for the detection of that transition to be possible. If the radial size of the indenter is too large, the deformation could remain elastic for the entirety of the loading range. The elastic modulus of the sample material can be too low for the selected loading range resulting in the same issue of the indenter not imparting high enough forces over the contact area to initiate permanent deformation.

Not only is there a limitation on the maximum stress that can be imposed given a maximum load limit, radii size, and the elastic modulus of the sample material, but also, there is a lower contact depth limit on the detectability of an elastic plastic transitory event. There are two main factors that are involved with this limitation. For one, there is the condition of the surface itself. The roughness of the sample surface can become a detriment if the roughness is at the scale of the size of the indenter itself. The stress field equations assume a perfectly smooth surface, and an infinite elastic half-space. This condition is obviously violated if the area of contact of the indenter does not dwarf the size of the surface perturbations. The second source adding to the lower contact depth limit of detectability is the intrinsic dynamics of an

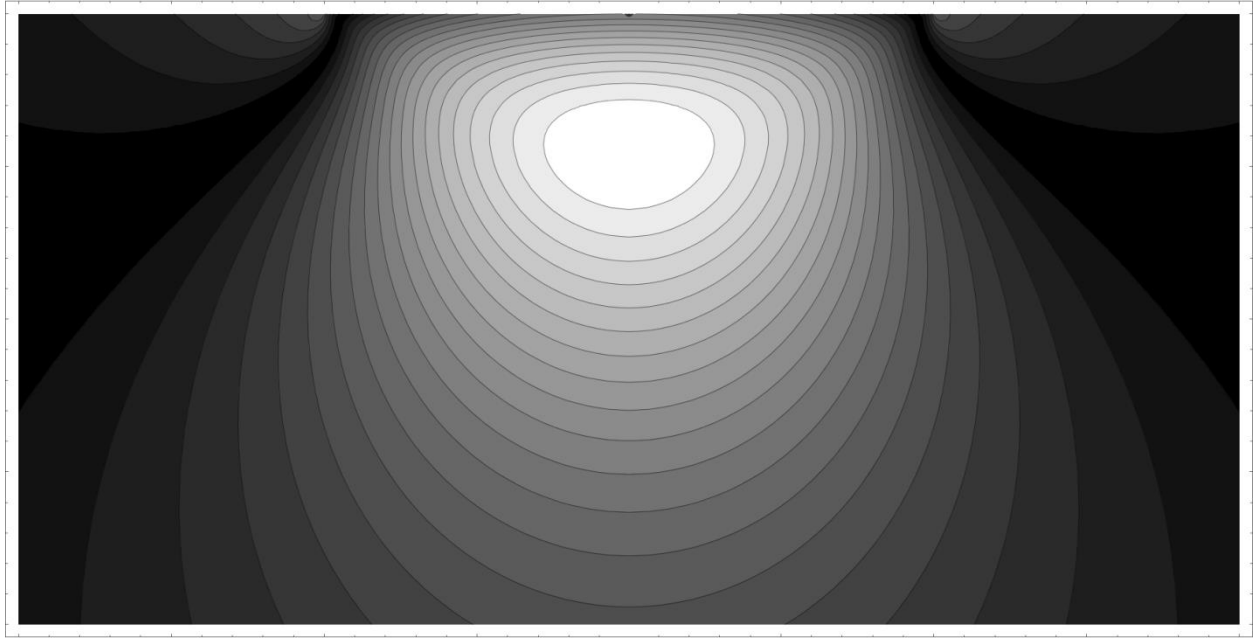


Figure 3.4: The elastic shear stress field developed beneath the contacted surface during spherical indentation. Lighter shades indicate higher shear stresses. The maximum shear stress for $\nu = 0.18$ occurs at a relative depth of $z/a \approx 0.44$ where $r/a = 0$.

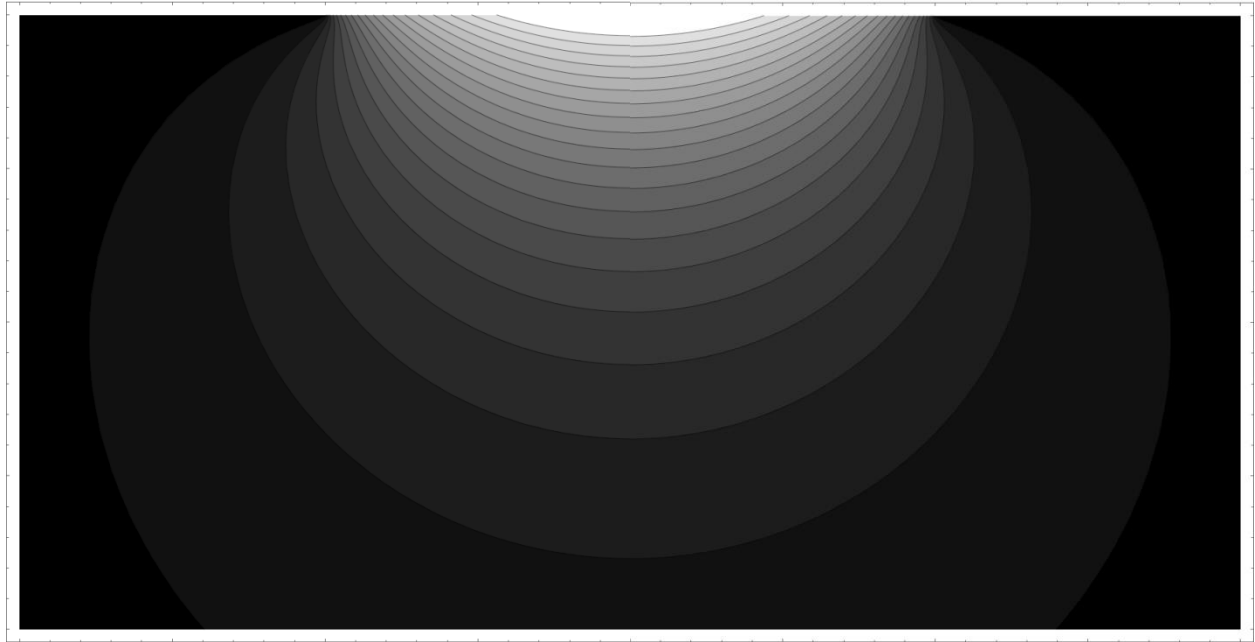


Figure 3.5: The elastic hydrostatic stress field developed beneath the contacted surface during spherical indentation. Lighter shades indicate higher shear stresses. The maximum hydrostatic stress occurs at the center of the surface.

instrumented indenter outfitted with continuous stiffness measurement capability. This involves a frequency lock-in amplifier which oscillates the force during load application. This function takes time to ramp up to the values defined for the test. For example, an oscillation with a flat amplitude of 5 nm wouldn't even be making constant contact with the surface initially. Therefore, in order for the dynamics to stabilize to a constant specified value and for constant contact with the surface to be maintained, there is an initial period where the amplitude ramps up and the properties derived from the dynamics during that period are invalid. The depth where dynamic stability is achieved varies based on the elastic properties of the sample material, the dynamic amplitude ramp rate, the maximum dynamic displacement, the dynamic gain, the indenter size, and the differing actuator dynamic properties. Fig. 3.6 depicts the dynamic stabilization for fused silica. The dynamic displacement limit is reached at a depth of ~50 nm for the 3.2 μm radius indenter.

A lower contact depth limit of yield detection in practical terms cautions that materials with high elastic moduli may fall below the detection limit when paired with an indenter with too small of a radius. At the same contact depth and indenter radius of curvature, a material with high elastic modulus will be supporting higher contact pressures than a lower modulus material. Fig. 3.7 and Fig. 3.8 show the range of applicable elastic moduli and mean contact pressure at yielding (approximately the yielding stress) for the three tip radii used. If a material's mechanical properties fall within a shaded swath, it is ensured the transition to yielding will be contained in the loading range accessible by the actuator (50 mN or 1000 mN).

Determining the true dimensions of the indenter

Knowing the physical dimensions of the indenting spheres is crucial to obtaining an accurate estimate of the stress state developed through contact. The analytical equations reflect this fact. The nominal, manufacturer-supplied, values for the radii of the indenters may not be representative of the true values. Indenters that are fashioned out of diamonds have anisotropic

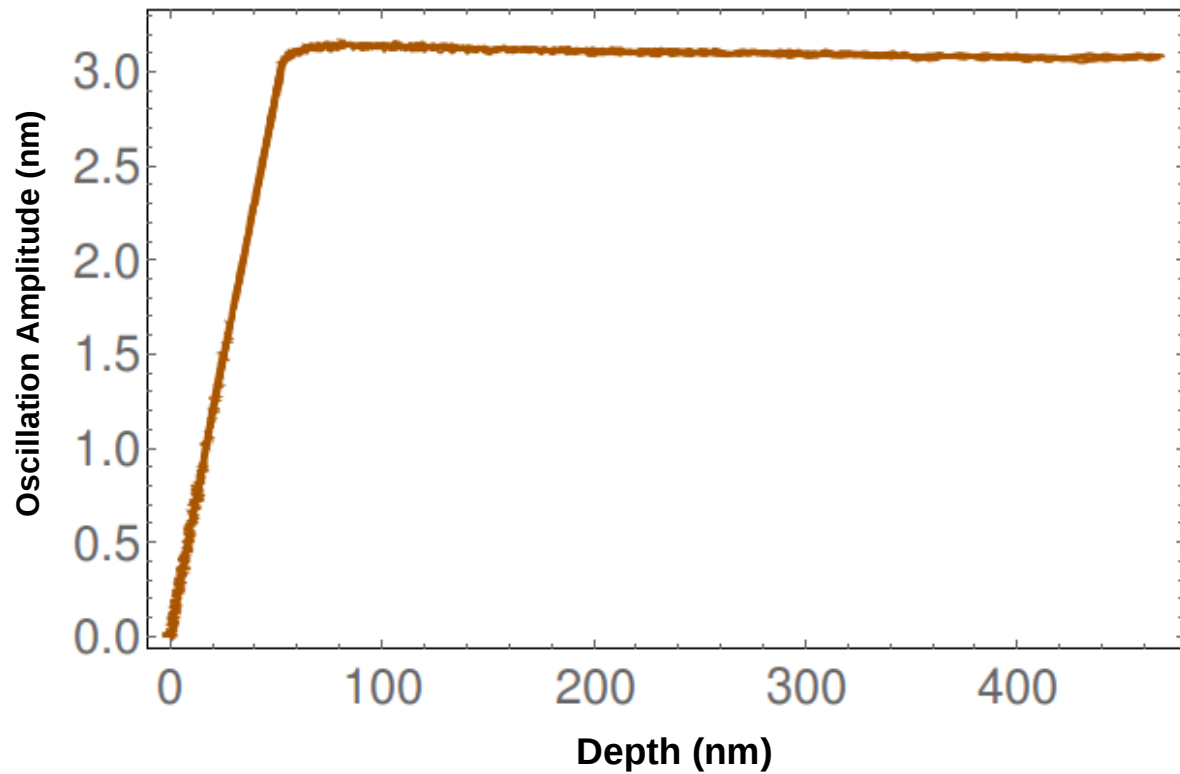


Figure 3.6: Dynamic amplitude of oscillation versus depth of indenter displacement for fused silica using the 3.2 μm radius tip. The target held amplitude is 3 nm. Values derived from the S^3/P are dubious prior to reaching 100 nm because of the rapidly changing amplitude.

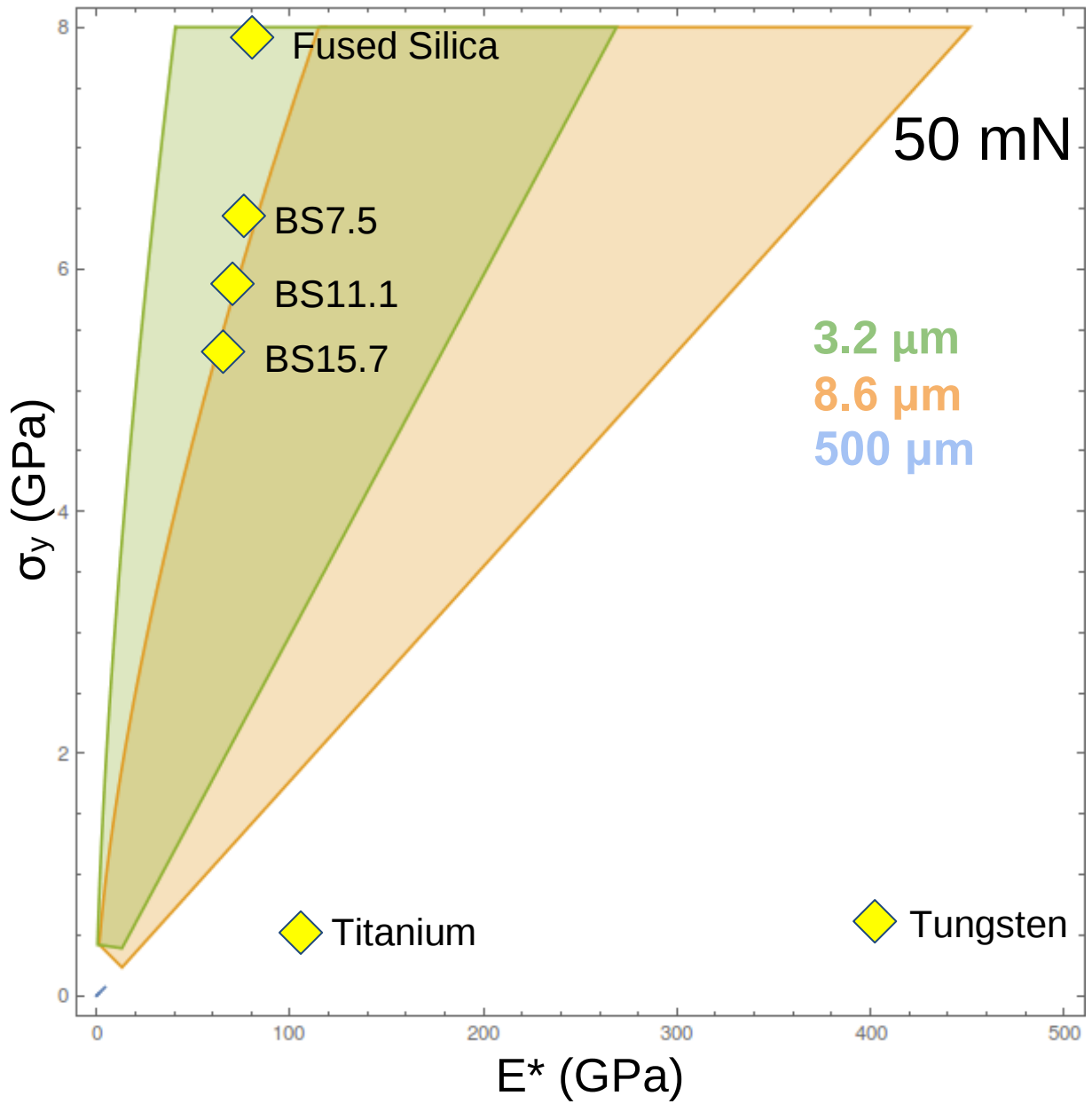


Figure 3.7: Swaths of accessible mean contact pressure and effective modulus pairs for the 50 mN actuator with a 50 nm low detectability floor. The swaths are color-coded according to the radius size of the indenter. The yellow diamonds mark the materials tested in this work.

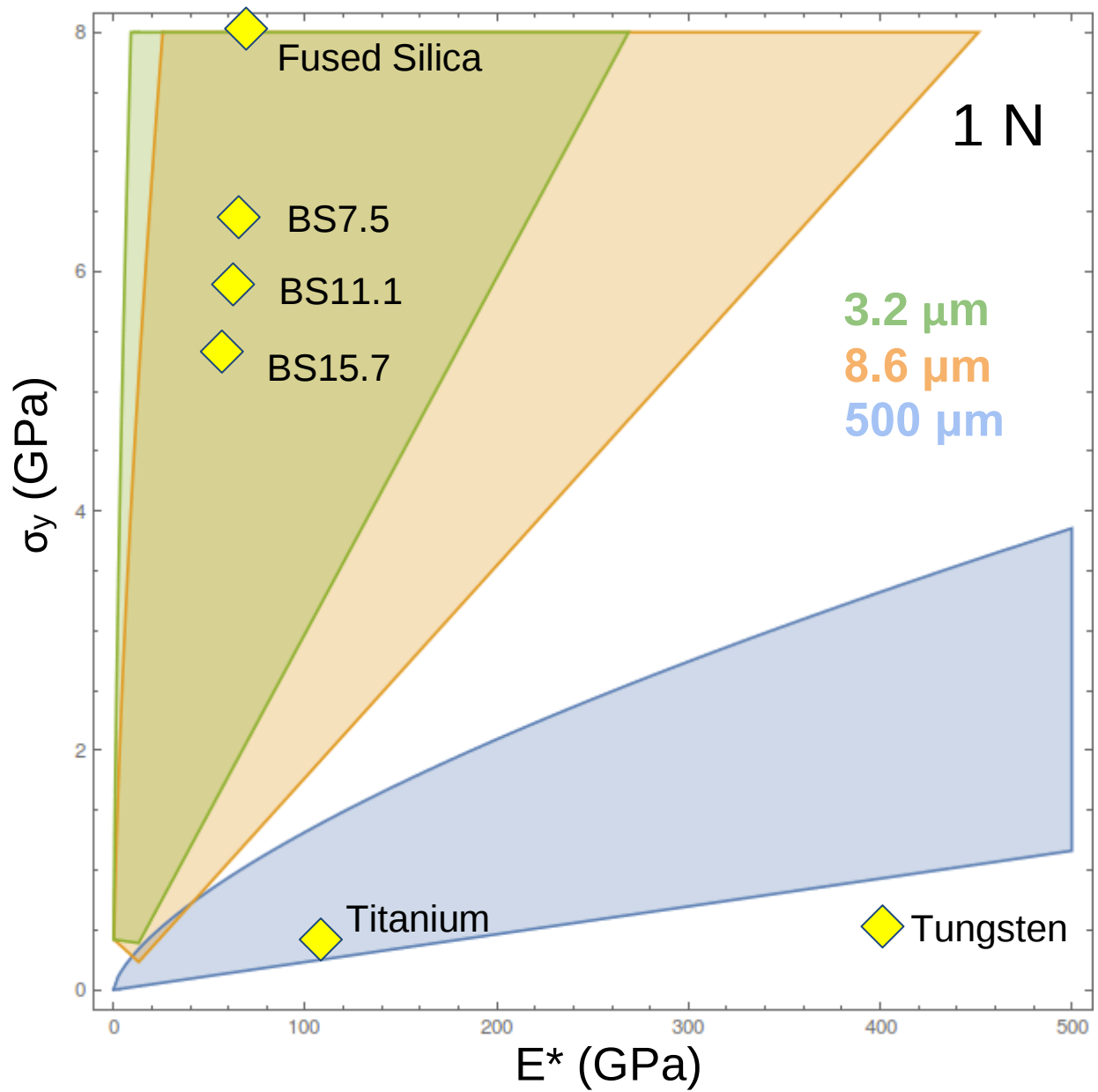


Figure 3.8: Swaths of accessible mean contact pressure and effective modulus (Equation 3.2) pairs for the 1000 mN actuator and with a 50 nm detectability floor. The swaths are color-coded according to the radius size of the indenter. The yellow diamonds mark the materials used in this work. If the diamond falls within a color-shaded region, elastic to plastic transition should be in the detectable range.

proclivities that give rise to uneven polishing rates and add overall difficulty in forming a consistent radius of curvature. Not only could the stated value be spurious, but the radius of curvature when analyzing different segments of the tip's surface could vary. For example, a SEM image of the nominally 14 μm radius indenter is shown in Fig. 3.9. A circle is drawn on the image as a dimensional fidelity test. However, the size of a drawn circle that attempts to fit the tip profile can vary, resulting in arbitrary determination of an accurate representative radius for the interested depths of contact. Directly measuring the tip in this way is often futile. Here, with knowledge of the elastic properties of a calibration material, the radius can be measured indirectly. Fitting an ideal elastic spherical indentation response with a given elastic modulus of the target material to an elastically maintained contact portion of a load-displacement curve allows for the radius to be solved for using Equation (3.4). The advantage of this process is it reveals contact information precisely over the intended testing range. For instance, in the case of the diamond spherical indenters employed in this work, the rounded tip is fashioned onto a cone. Thus, there is a region that could be reached at a high enough contact depth whose profile is defined more by a cone angle instead of a radius of curvature. However, since contact is occurring at depths much smaller than the radius of the rounded end, the cone-shaped portion plays no role in the contact. The radii of the diamond indenters were found by calibrating to a fused silica reference sample ($E = 72 \text{ GPa}$). Fig. 3.10 demonstrates the curve-fitting calibration overlaying the fitted curve to the real loading data. For the two rounded diamond indenters, 5 μm and 14 μm nominal radii turn out to be 3.2 μm and 8.6 μm calibrated radii values respectively for the contact depth range accessed in this work.

Verifying indenter area of contact

The potential for a size-dependent feature to affect estimated yield stress should not be dismissed. Indentation hardness, being a measurement of resistance to plastic deformation, is a correlated analog of yield stress. Hardness has been shown to exhibit size-dependent effects in

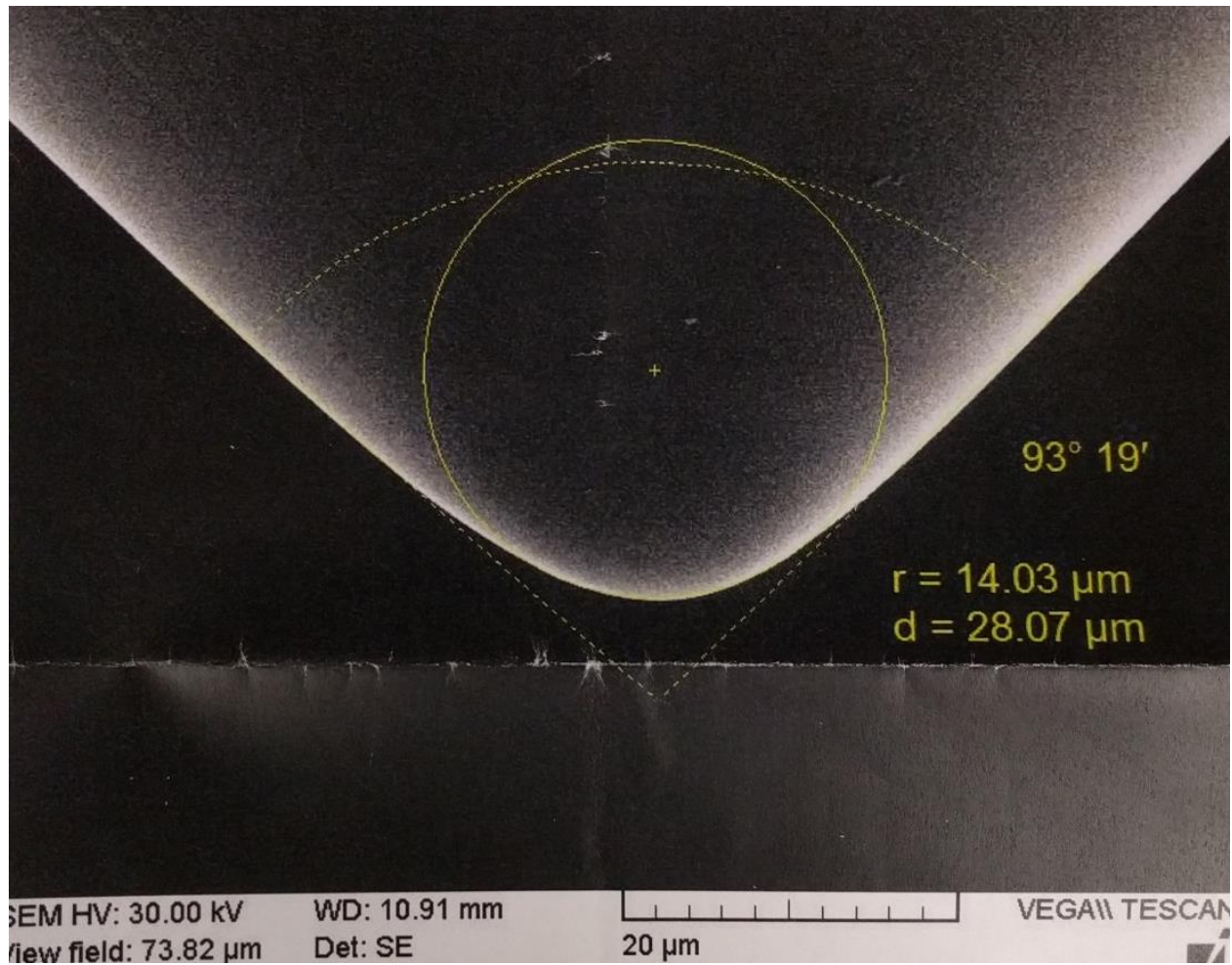


Figure 3.9: SEM image of the nominally 14 μm radius tip demonstrating that the overlaid sphere radius does not necessarily accurately represent the true curvature of the tip.

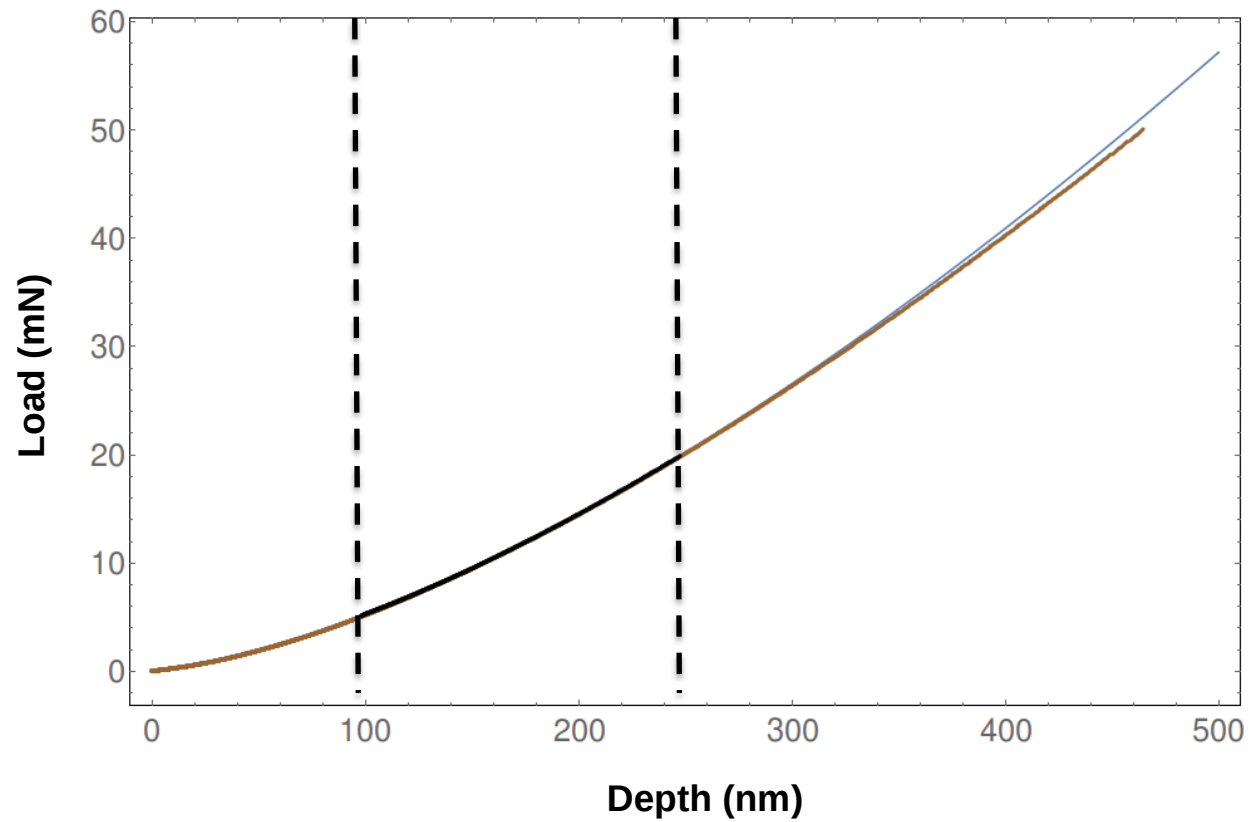


Figure 3.10: A fitted load versus displacement curve shown for fused silica indented with the nominally 5 μm radius establishes a correct description of the tip geometry. The brown curve is the actual load and displacement data, while the blue curve is based on a least squares power law fit of the data outlined in black and bounded by the two vertical dashed lines.

some materials, so it could be anticipated that the yield stress could carry similar size effect characteristics. Therefore, knowing potential size-dependent characteristics of the target material would be helpful in the event the size of the contact triggers undesirable mechanisms.

Frame stiffness and area function calibration

Another factor to consider in obtaining accurate contact stiffness and analogously accurate yield stress measurements is the testing frame stiffness. Most standard procedures to determine the frame stiffness take advantage of the self-similarity of pyramidal-based indenters. A correctly calibrated frame stiffness results in a constant stiffness squared over load value. This option is not afforded by using spherical geometry for an indenter. Yet, the overall frame stiffness should remain consistent despite differences in tip geometry. The value for the frame stiffness obtained through tip contact area calibration for a Berkovich tip ($3.0 \times 10^6 \text{ N/m}$) remains valid for a spherical tip contacting the same sample. This process was followed to obtain a universal frame stiffness value. The area function of the diamond Berkovich tip was calibrated according to the published elastic properties of the fused silica reference material ($E = 72 \text{ GPa}$) a constant stiffness squared over load value. Dual-sourced S^3/P curves will be vertically offset if an improper frame stiffness value or non-representative area function for the indenting sphere are used.

Loading rate

All tests were performed using a constant loading rate to load ratio of 0.2 s^{-1} . Strain rate sensitivity was not explored, and all materials were evaluated under nominally quasi-static loading conditions. Departure from these conditions is not covered.

Application of the yield stress determination method to fused silica and soda-lime silicate glass

Materials and experimental details

The above-outlined technique to estimate yield stress was applied to two inorganic glasses: a pure fused silica glass (HPFS® IG, Corning, Inc., Corning, NY, USA) and a soda-lime silicate glass (Starphire®, Vitro, S.A.B. de C.V., San Pedro Garza García, Mexico). These two glasses were chosen to demonstrate application of the newly developed method primarily because each is representative of prototypical anomalous and normal glasses respectively. Additional material information on the soda-lime silicate glass can be found in [86].

A series of nine indentations per peak load and per spherical tip size were executed for each glass with an iMicro Nanoindenter (Nanomechanics Inc., Oak Ridge, TN, USA) using rounded diamond cones with 3.2 μm and 8.6 μm radius tip sizes determined from the elastic indentation response of fused silica, which is used as a calibration standard since its elastic moduli are known. The peak loads ranged from 10 mN to 40 mN with a constant loading rate to load ratio ($\dot{P}/P$) of 0.2 s^{-1} . This allows a wide range of critical mean contact pressures to be accessed while also addressing potential size effect influences. The pressures accessible with these radii and peak loads are within the range where permanent deformation and potential densification have been demonstrated to occur in high pressure hydrostatic tests [25]. The unloading stiffness of the contact was measured using continuous stiffness measurement techniques driven at 100 Hz with constant 3 nm amplitude through the critical range of contact depth. The loading stiffness was derived using an interpolation scheme and subsequent differentiation of the interpolated load-displacement function. All of the tests occurred under standard atmospheric pressure and temperature. The sample surfaces were prepared in non-aqueous mediums. Detailed analysis of the polishing procedure is found in Chapter IV.

Result of method application

Perhaps the most direct route to sensing the formation of a permanent impression is through analysis of loading and unloading curves. Ideally, if non-recoverable deformation occurs, load-displacement hysteresis will develop. Incremental tests of increasing maximum load show this progression. The result of using the simple criterion of hysteresis development in fused silica is shown in Fig. 3.11. It is clear that at the two highest peak loads of 20 mN and 40 mN, hysteresis is present. However, when comparing the two lowest peak loads of 10 mN and 20 mN, there is uncertainty as to whether hysteresis has developed in either; there is no clear separation of unloading and loading curves within the experimental uncertainty of the measured displacements. Even when using a highly sensitive instrument, the experimental uncertainty renders precise determination of the onset of permanent deformation implausible using just load-displacement hysteresis as an indicator, again running into the same issues shared by prior investigators regarding the seemingly intractable nature of the gradual transition and requires multiple tests over a range of loads.

The new approach to sense the formation of a residual impression is demonstrated for fused silica in Fig. 3.12 and Fig. 3.13 giving an experimental confirmation of the idealized response shown in Fig. 3.2 for two indenter sizes (3.2 μm and 8.6 μm). Two sets of curves representing two different means of obtaining the stiffness used in the invariant elastic parameter S^3/P are plotted simultaneously. The two distinct regimes appear as theoretically predicted: one where the two curves track with each other, and the second where the curves are divergent. The divergence point is the indicator for the onset permanent deformation due to changes in the effective radius of curvature pair between the indenter sphere and the newly formed permanent residual impression.

The transition point is visually enhanced when observing just a singular test in Fig. 3.12b. and Fig. 3.13b. Already this method has the advantage of only requiring a single

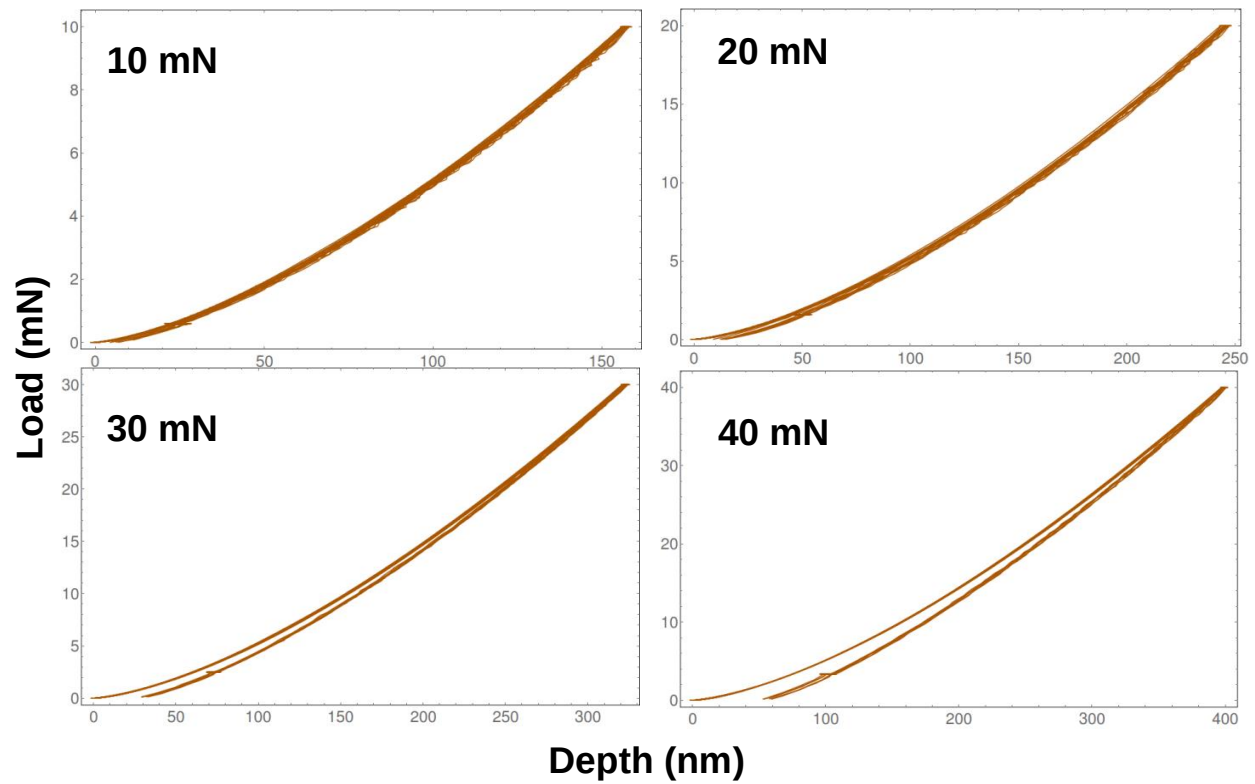


Figure 3.11: Spherical load-displacement curves of fused silica at peak loads ranging from ± 10 mN to 40 mN showing development of hysteresis as the peak load is progressively increased beyond a critical load.

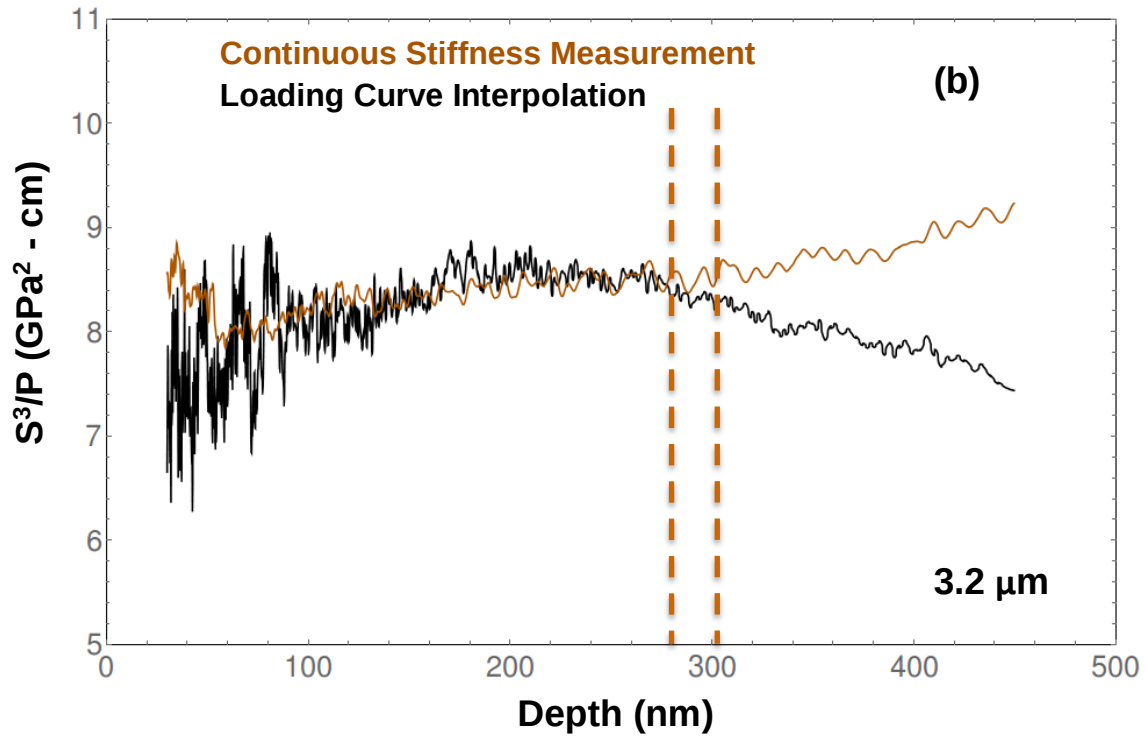
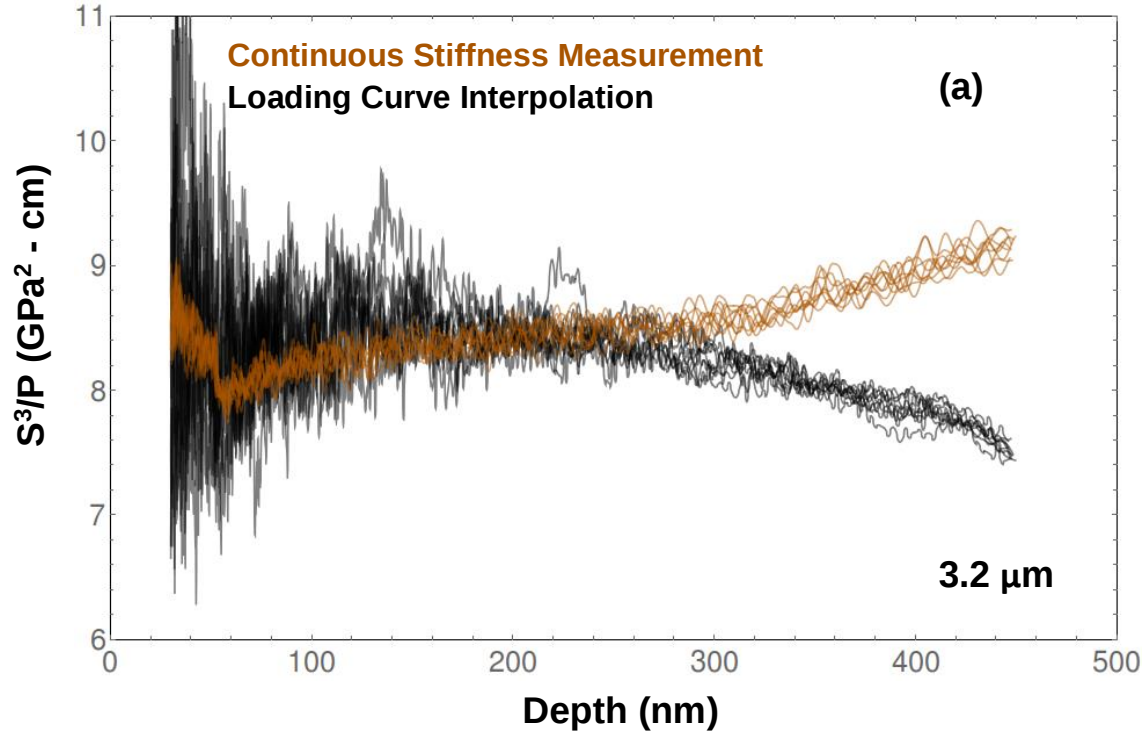


Figure 3.12: (a). S^3/P parameter for nine 3.2 μ m indentation tests of fused silica plotted simultaneously for each stiffness source: continuous stiffness measurement (brown) and loading curve interpolation (black). (b). A single indentation test taken from one of the nine samples. ± 10 nm uncertainty bounds are applied at the point of yielding.

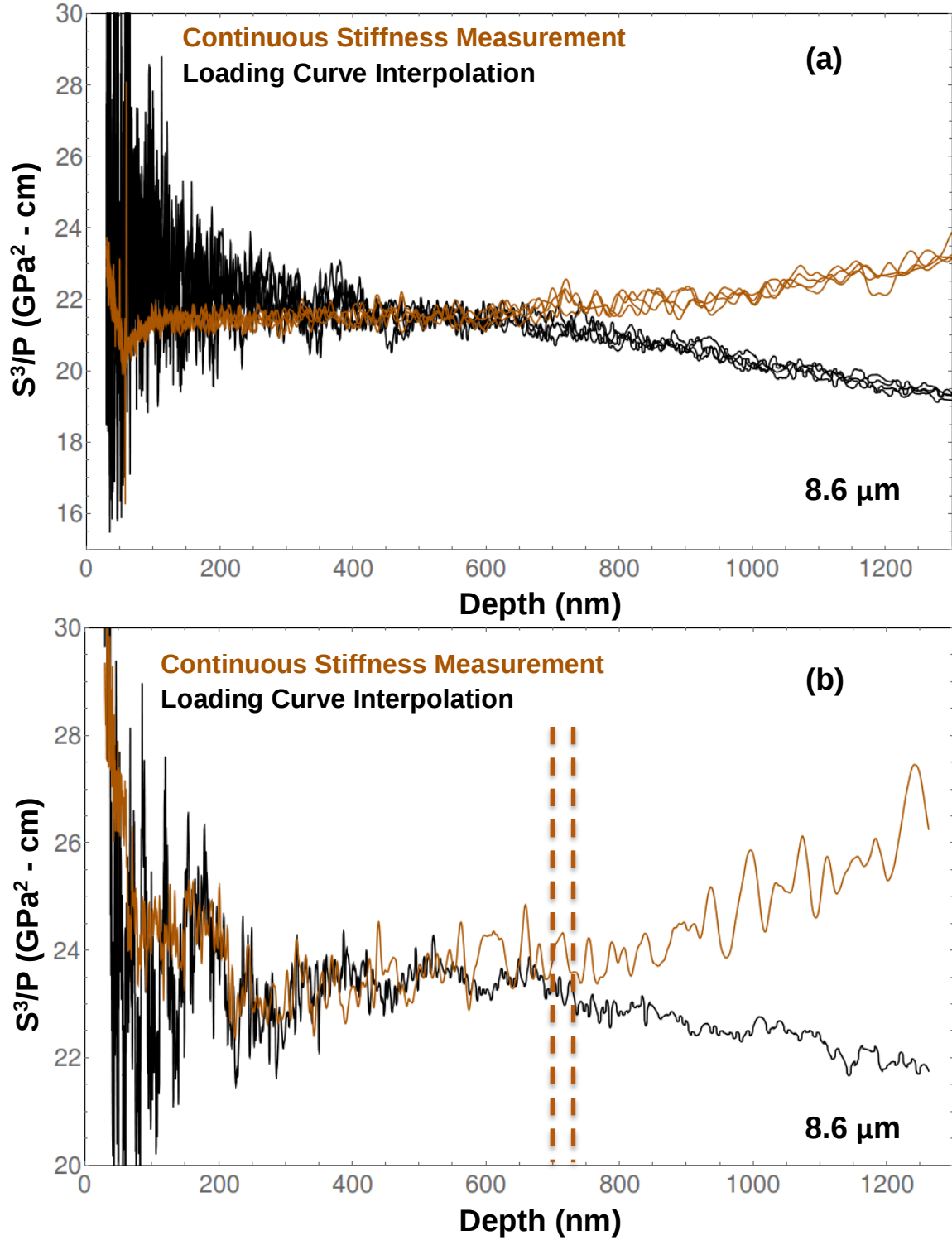


Figure 3.13: (a). S^3/P parameter for five $8.6 \mu\text{m}$ tests of fused silica plotted simultaneously for each stiffness source: continuous stiffness measurement (brown) and loading curve interpolation (black). (b). A single indentation test taken from one of the five samples. $\pm 10 \text{ nm}$ uncertainty bounds are applied at the point of yielding.

chosen peak load compared to the multiple increments needed for hysteresis analysis. The load-displacement pair associated with the onset of permanent deformation for fused silica (23.3 mN, 290 nm) is found graphically. 10 nm uncertainty bounds are added to provide a measure of the effect of potential subjective variance in determining the point of divergence and consequently the estimated yield stress. Once the critical load-displacement state is found graphically from the first appearance of divergence of loading and dynamic unloading derived S^3/P curves, it must be converted into principal stress terms for use in applicable constitutive yielding relations. The ratio between mean contact pressure and the yield stress is near unity for Poisson ratios near 0.2. The final yield stress value determined for fused silica using this technique is 8.1 ± 0.2 GPa using the $3.2 \mu\text{m}$ radius indenter.

The Starphire S^3/P yield point determination curves are shown in Fig. 3.14 and Fig. 3.15. The yield stress determined for the soda-lime silicate glass is 6.1 ± 0.2 GPa using the $3.2 \mu\text{m}$ radius indenter. Two differences between the form of the curves between fused silica and soda-lime silicate are the depth of the divergence point and the slope of the divergent section of the curves. The shallower divergence point depth observed for the soda-lime silicate glass is related directly to the lower relative yield stress since the elastic moduli of the two glasses are similar. Analysis of what the rate of progression of the S^3/P curve represents after yielding is outside the scope this work, which is focused more on the yielding event itself, but it could be related to a rate of growth for the size of an impression. The wider mouth of the soda-lime silicate divergent S^3/P parameter compared to fused silica could again support another distinction between the mechanical behavior of normal and anomalous glasses. The estimations of yield stress for each glass and indenter size are presented in Table 3.1. The final determined yield stress values did not change based on the size of the two indenting radii, within the measurement certainty.

Theoretically, the S^3/P parameter should be invariant in the elastic regime if the effective modulus and radius of curvature of the indenter-surface couple are assumed constant.

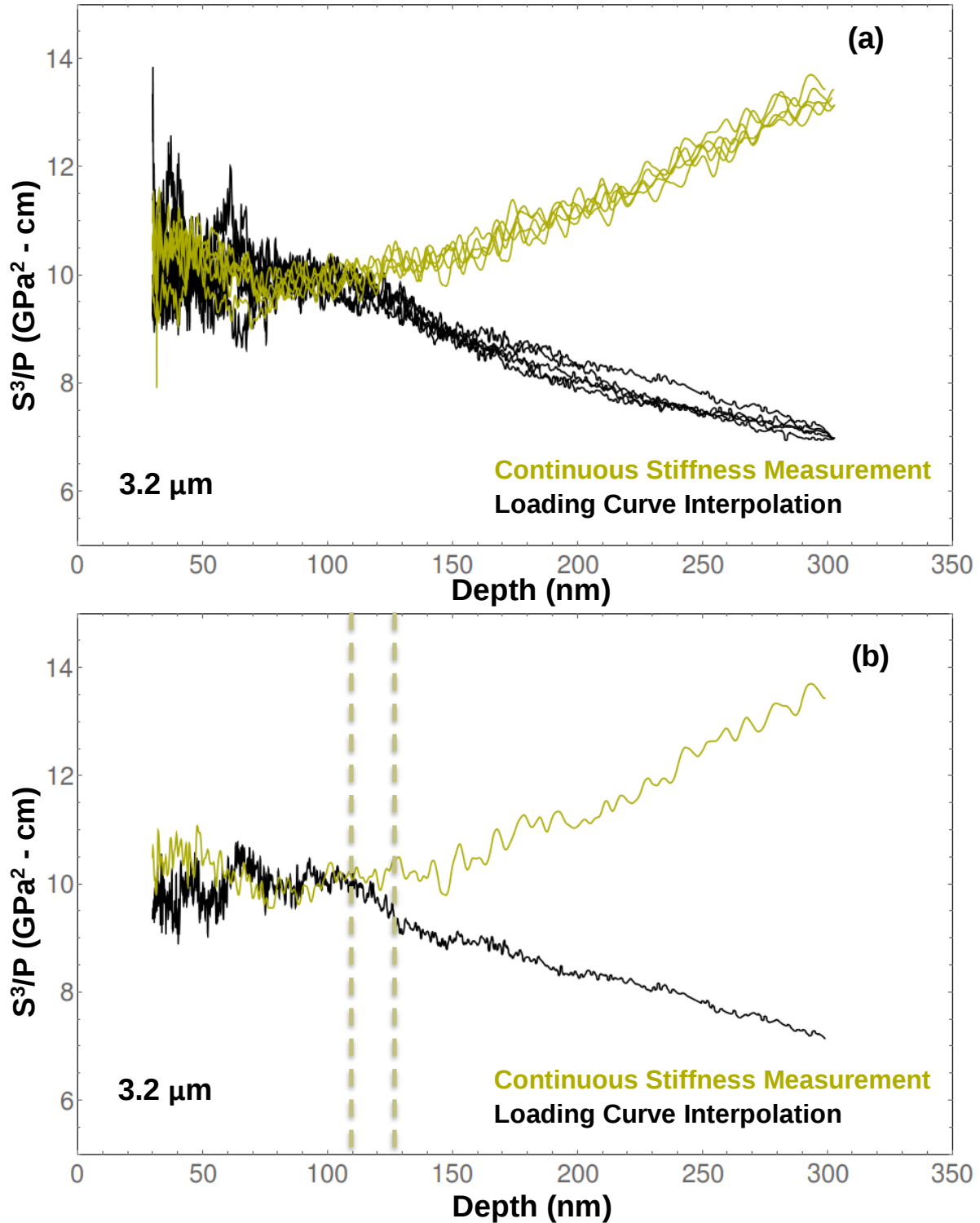


Figure 3.14: (a). The parameter S^3/P versus displacement is plotted using nine separate $3.2 \mu\text{m}$ spherical indentations of soda-lime silicate using dynamic continuous unloading stiffness (yellow, rising after divergence) and stiffness derived from the slope of the loading curve (black, falling after divergence). The point of divergence indicates the depth of penetration where yielding initiated. (b). A single test out of the nine is shown with $\pm 10 \text{ nm}$ dashed uncertainty range about the yielding onset point.

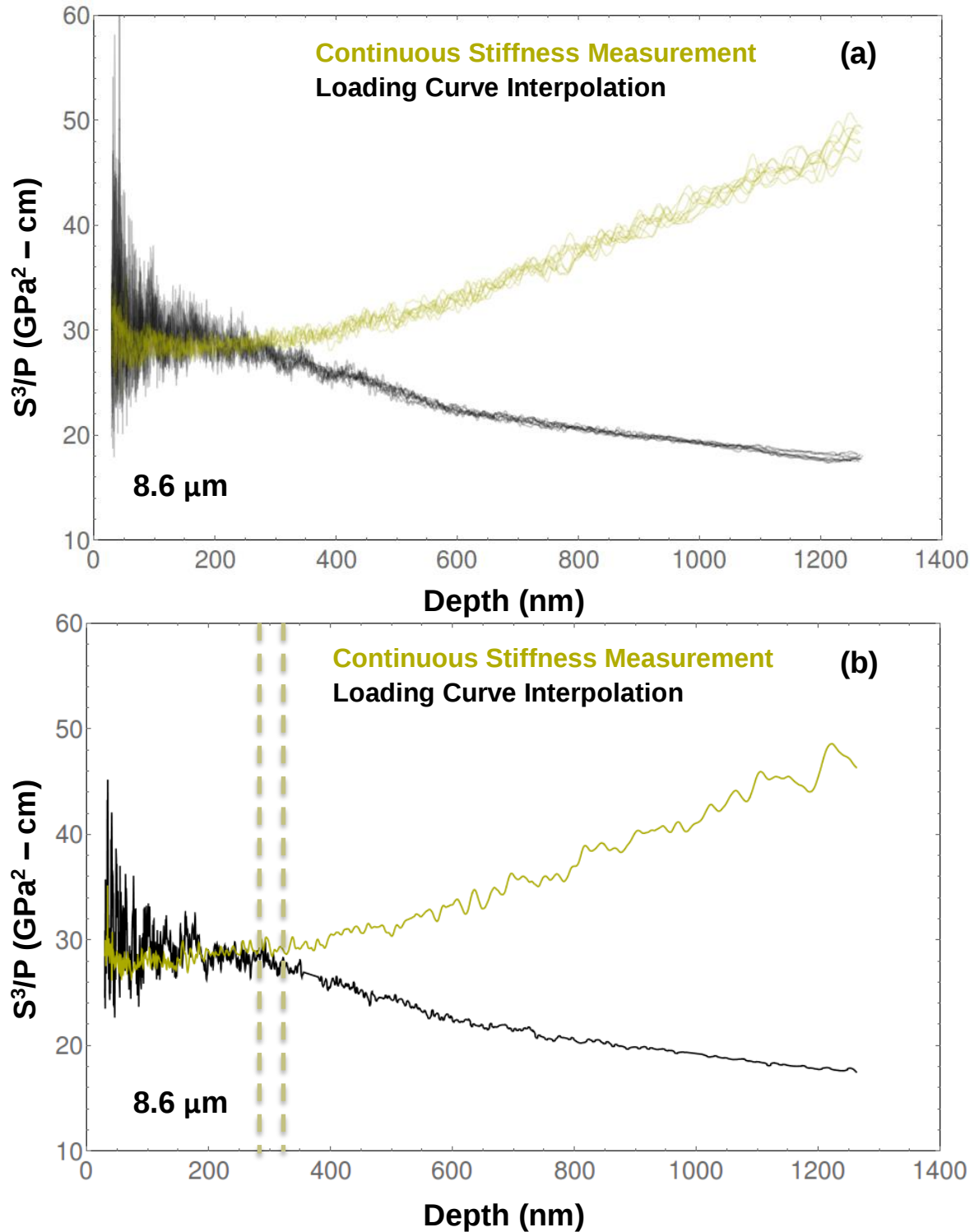


Figure 3.15: (a). The parameter S^3/P versus displacement is plotted using nine separate $8.6 \mu\text{m}$ spherical indentations of soda-lime silicate using dynamic continuous unloading stiffness (yellow, rising after divergence) and stiffness derived from the slope of the loading curve (black, falling after divergence). The point of divergence indicates the depth of penetration where yielding initiated. (b). A single test out of the nine is shown with $\pm 10 \text{ nm}$ dashed uncertainty range about the yielding onset point.

Table 3.1: Yield Stress Estimated Using New Technique

Material	Indenter Radius (μm)	Estimated Yield Stress Indentation Method	Compressive Yield Stress
Corning HPFS® Fused Silica IG	3.2 8.6	8.1 ± 0.2 GPa 8.2 ± 0.1 GPa	N/A
Vitro Starphire® Soda-Lime Silicate	3.2 8.6	6.1 ± 0.2 GPa 6.1 ± 0.1 GPa	N/A
Materion Vit 106a Bulk Metallic Glass	8.6	6.5 ± 0.2 GPa*	1.7 GPa
Electro-Polished Tungsten Mechanically Polished Tungsten	8.6 N/A	~8 GPa* N/A	N/A 550 MPa
Titanium	500	430 ± 30 MPa	380 MPa

*Exhibited pop-in behavior

However, experimentally, fluctuations of the parameter are observed within the elastic regime, prior to divergence. These fluctuations are caused primarily by high experimental noise at the smaller depths of penetration. If the loading and dynamic unloading S^3/P curves match one another that means no detectable permanent impression has yet formed. Larger initial changes with the dual S^3/P curves points to surface or tip inconsistencies.

Repeatability and error analysis

The reproducibility of yield stress measurement is contingent upon consistent surface characteristics. In other words, if the surface that is being tested has intrinsic heterogeneity, then this will correspond to variation of yield stress measurement. The repeatability of this measurement method is demonstrated in Fig. 3.16a by load-displacement data and Fig. 3.16b by the dynamic S^3/P parameter. Nine tests of fused silica are plotted simultaneously in each figure. 10 nm uncertainty bounds are included in the final tabulations to provide a measure of the effect of potential subjective variance in determining the point of divergence and consequently the estimated yield stress. Once the critical load-displacement state is found graphically from the first appearance of divergence of loading and unloading derived S^3/P curves, it must be converted into principal stress terms for use in applicable constitutive yielding relations. Budgeting for a 10 nm error results in ± 0.2 GPa uncertainty range in the estimation of the yield stress for the $3.2\ \mu\text{m}$ radius tip, an order of magnitude better performance compared to techniques laid out in Swain and Hagan [71].

Discussion of Theoretical Assumptions

There are many assumptions and potential parasitics that must be addressed when using the new technique that could be the source of real changes in S^3/P , separate from experimental noise. It is assumed that the shape of the indenter is well defined with no large defects or discontinuities such as chipping, but at low depths, the influence of even small

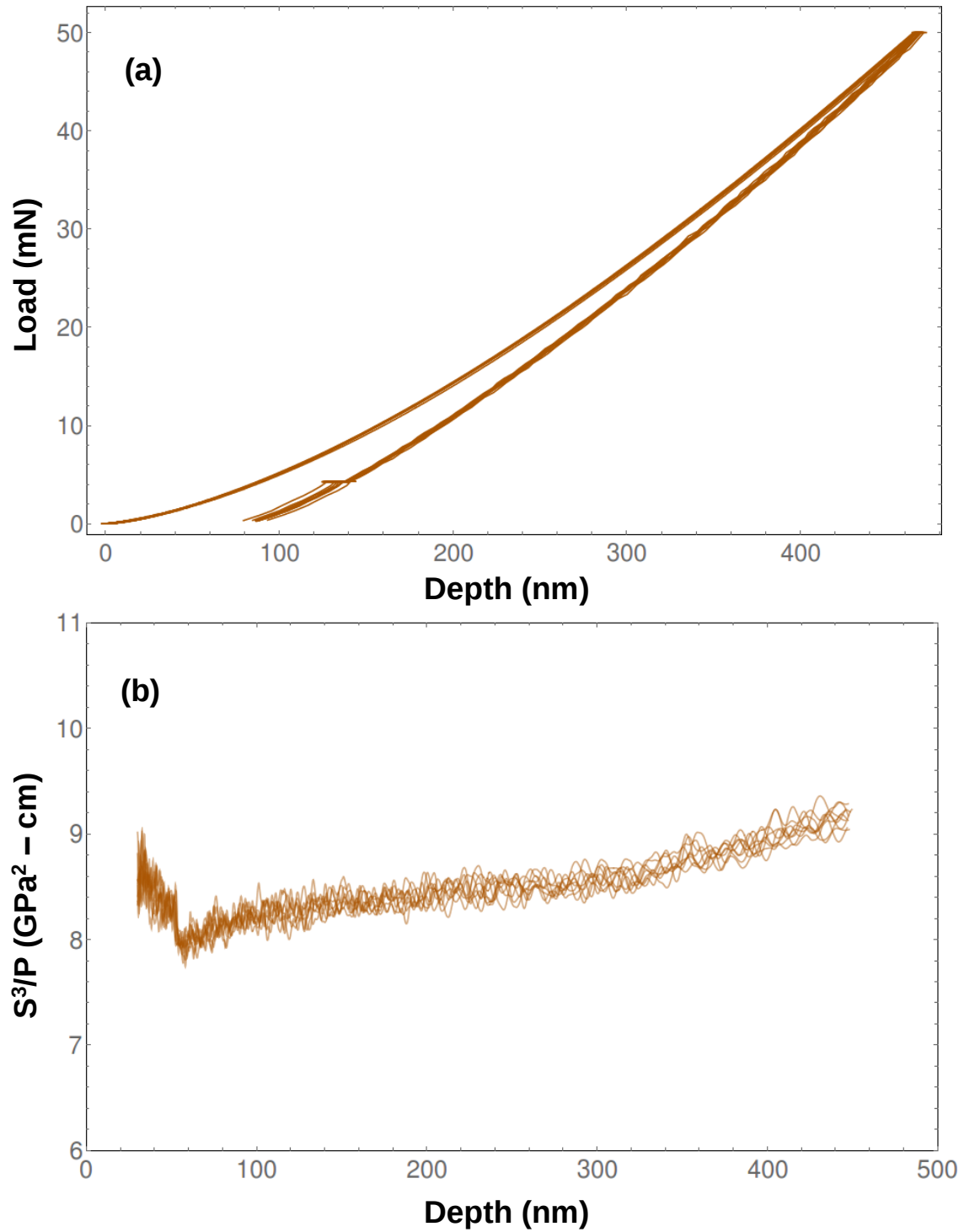


Figure 3.16: (a). Multiple load versus depth of indenter displacement curves for fused silica demonstrating high repeatability and low variance between tests. (b). Multiple dynamically-sourced S^3/P curves showing the level of noisiness of the parameter.

irregularities can become greatly magnified.

Tip defects

The tip is assumed to be well defined and described by a singular radius of curvature for the range applicable contact depths. Tip radius calibration is a vital requirement for accurate yield stress measurement. The Hertzian elastic contact and stress field equations are a first approximation of truly spherical contact. This approximation simplifies the model the contact of contact to a parabola of revolution. Small contact depths relative to the radius of curvature of the indenter must be maintained at all times during contact in order to minimize the differences between a parabola of revolution and a sphere. The total depth during the course of these experiments never exceeded a fifth of the radius of curvature of the indenting tip.

Frictional influences

Friction is assumed to have a negligible effect on the onset of yielding. This assumption is validated through prior finite element modeling comparing a sticking indenter to a frictionless one [87]. Heating or other stress relaxing processes potentially caused by the indentation process are assumed to be insignificant.

Pre-existing stresses

In the same study [87], residual stresses were found to affect the average contact pressure and normalized contact area, while the contact stiffness was independent of the pre-existing stress state. Although tensile stresses do develop that can lead to crack formation, crack-free spherical indentations were produced at loads that were still sufficient to cause yielding. Any complications that could arise from the presence of cracks should be avoided by placing indents outside the zone of influence of a crack just as indents are spaced apart to avoid interference.

Sample surface roughness

The sample surface must undergo thorough planarization to reduce a real surface's deviation from idealized smoothness. Excessive roughness typically becomes apparent through variation in load-displacement curves when comparing multiple indentations. If the scale of the roughness approaches the scale of the contact, test to test reproducibility is hampered along with the reliability of stiffness measurements, especially at low contact depths.

Choice of yield criteria and mechanisms

An important aspect to consider in order to form accurate estimation of the yield stress is the choice of a yield criterion that reasonably describes the underlying operating deformation mechanism in the sample material. For example, if it is known that the target material has cohesive frictional forces, then a matching yield criterion which incorporates that property should be selected.

Apparent deformation

The underlying premise of using spherical indentation to assess yielding phenomena is dependent upon when during the course of loading permanent deformation becomes detectable. It is conceivable that due to the maximum shear stress occurring at a finite depth beneath the surface, there could be a lag between when the material begins to yield beneath the surface and when such permanent deformation becomes apparent and detectable at the surface as a residual impression (i.e., the force of actual permanent deformation initiation is less than that associated with surface-located permanent deformation detection). Therefore, estimations of the mean contact pressure and resulting conversions to a yield stress may be overestimations.

Insensitivity to small-volume elastic modulus changes

When analyzing the variables in Equation (3.6), there are two ways in which the S^3/P parameter can change: changes to the reduced elastic modulus, and changes to the effective

radius of curvature of the contact. Deconvolution of the relative effect of each could be problematic. Although the elastic modulus of fused silica has been shown to exhibit anomalous behavior with increased applied hydrostatic pressure (initially increasing compressibility and decreasing elastic moduli) [88], evidence from Oliver and Pharr shows instead a constant effective modulus during indentation for a variety of materials, including fused silica [53]. This is because the elastic response that is being sampled during indentation involves a volume of material that extends well beyond the immediate contacted region. Far-reaching effects of the elastic hinterland contribute to an averaging of measured elastic properties beyond the small actual volume of material that is being appreciably altered by the imposition of contact pressure. This tendency for collective contribution to elasticity coming from outside the immediate contact zone is further addressed in context to a film-like layer on a substrate in Chapter IV.

Testing the Veracity of the Method

In light of the discussion of associated assumptions and parasitics, a check of the veracity of the method and accompanying presuppositions was undertaken using a bulk metallic glass for which the yield stress can be independently measured in uniaxial compression tests. Without a way to directly test the bulk yield properties of glass conventionally, how can the numbers for yield stress be trusted as being accurate? The method must be verified independently with a different material whose yielding properties can be ascertained both through conventional techniques and through the novel indentation methodology explicated in this chapter to test if the values reasonably agree.

Materials and experimental details

Materials used to carry out verification of the method and its applicability beyond inorganic glasses included three metals: a zirconium-alloy-based bulk metallic glass (Vit 106a, Materion Corporation, Mayfield Heights, Ohio, USA), tungsten, and as-drawn high purity

polycrystalline titanium. In the first attempt to experimentally demonstrate the equivalency of the yield stress estimated using indentation and the yield stress obtained through conventional bulk uniaxial testing, the bulk metallic glass was subjected to compression testing according to ASTM E9 [89]. Specimens, ~ 10 mm tall, were machined to an aspect ratio of three. The other test materials were machined according to the same standard. Five compression tests of each sample were carried out and force versus crosshead displacement was recorded. Crosshead velocity was set to achieve a constant extension rate of 0.05 mm/min. An extensometer was not employed, so the true strain is unknown. Nevertheless, for this experiment, the only parameter that is sought is the yield stress, so true strain measurement was deemed to be extraneous.

The expected yield stress of titanium is lower compared to the BMG and thus necessitated using a sphere with a much larger radius (500 μm) to ensure that the critical elastic to plastic transition did not occur at too shallow of a contact depth for detectability. Large diamond tips are notoriously difficult and time-consuming to grind, owing to their extreme hardness, so a sapphire tip oriented along the c-axis of symmetry was used.

Results and discussion of veracity tests: BMG and tungsten compression

Although there is some level of similarity in structure and properties between fused silica, soda-lime, and bulk metallic glass, differences in deformation mechanisms (characteristic pop-ins and shear transformation zones for bulk metallic glass [90]) could falsify direct comparison. A collection of spherical indentation loading-displacement curves of the Vit 106a is provided in Fig. 3.17, and all exhibit distinct pop-in behavior at around 270 nm. The near instantaneous jump of displacement corresponds to a sharp transition from exclusively elastic deformation to plastic flow. The S^3/P curves displayed in Fig. 3.18 show the same sudden transition. Using the bulk metallic glass as a surrogate for silicate glasses to judge the equivalency of the onset of yielding between a conventional uniaxial compression method and the newly developed spherical indentation method failed. Shear bands around the bulk metallic

glass indent are visible in Fig. 3.19. Pan et. al. [91] postulated that the onset of yielding in metallic glasses in response to indentation contact occurs when a critical stress is reached resulting in a shear transformation zone cascading effect. With a reduced indentation length scale, the population of easily activated shear transformation zones and flaws in the stressed volume becomes low and yield stress increases, flow being controlled by heterogeneous nucleation of a shear band rather than propagation [92].

It is likely for this reason that there is such a large discrepancy in the yield stress found using conventional uniaxial compression displayed in Fig. 3.20 (1.7 GPa), and the yield stress computed corresponding to the first pop-in in the indentation shown in Fig. 3.17 (6.5 GPa). The localization of plasticity in the form of shear bands breaks one of the key assumptions inherent in the use of the maximum shear stress criterion, namely that the deformation mechanism be amenable to continuum mechanics descriptions. The search for a material that could meet those requirements was not trivial. A bridge between the indentation scale deformation and the bulk continuum had to be formed. Initially, it was assumed that the ideal material of choice would be one that retained the same amorphous character as the borosilicate glasses to which this effort at estimating the yield stress is ultimately directed. While the amorphous structure of the bulk metallic glass is homogeneous, the operative deformation mechanism revealed itself in the form of localized shear banding.

Yield stress is a continuum mechanics conception meaning that its value is intended to represent a material with properties that are continuous at any level. Nanoindentation, by

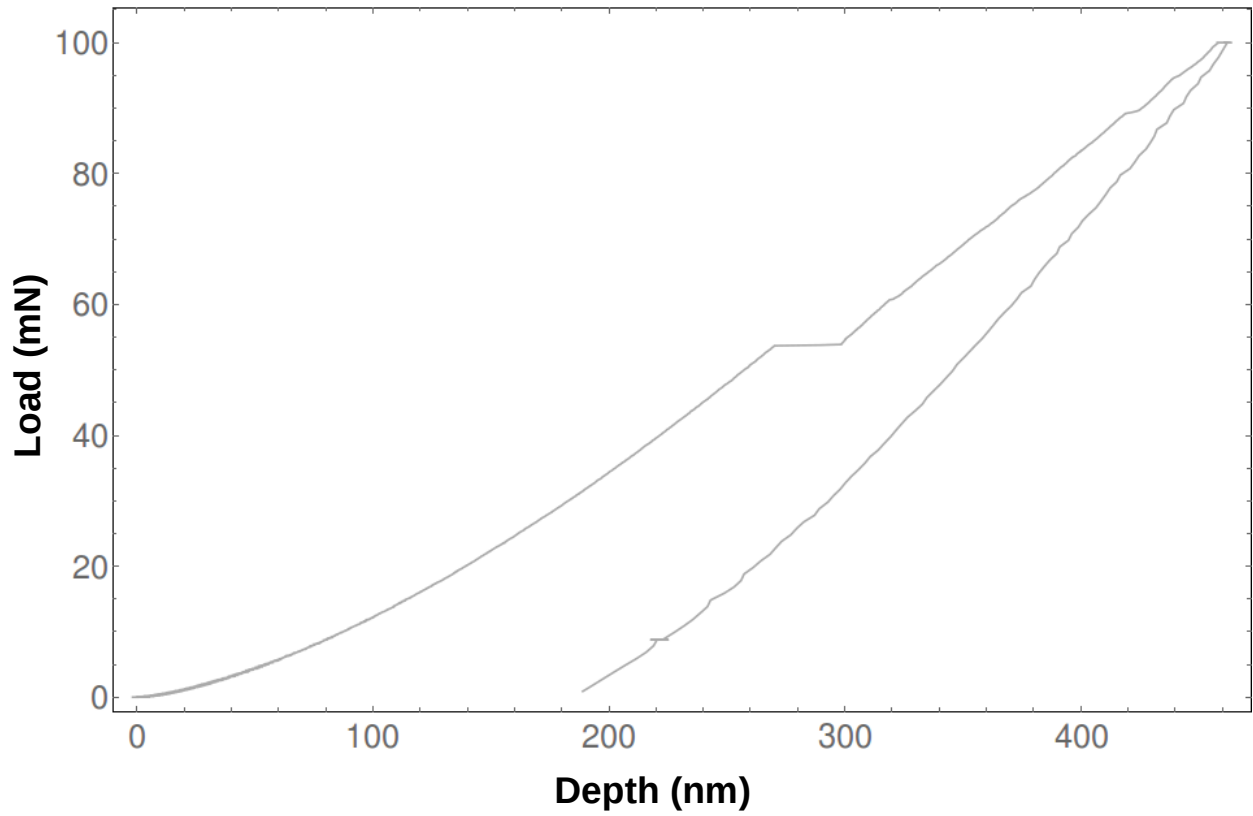


Figure 3.17: Spherical load versus depth of indenter displacement curve for Vit 106a BMG using an 8.6 μm radius tip. Elastic behavior prevails right up until the 270 nm mark where there is the first pop-in, a brief burst of discretized plasticity.

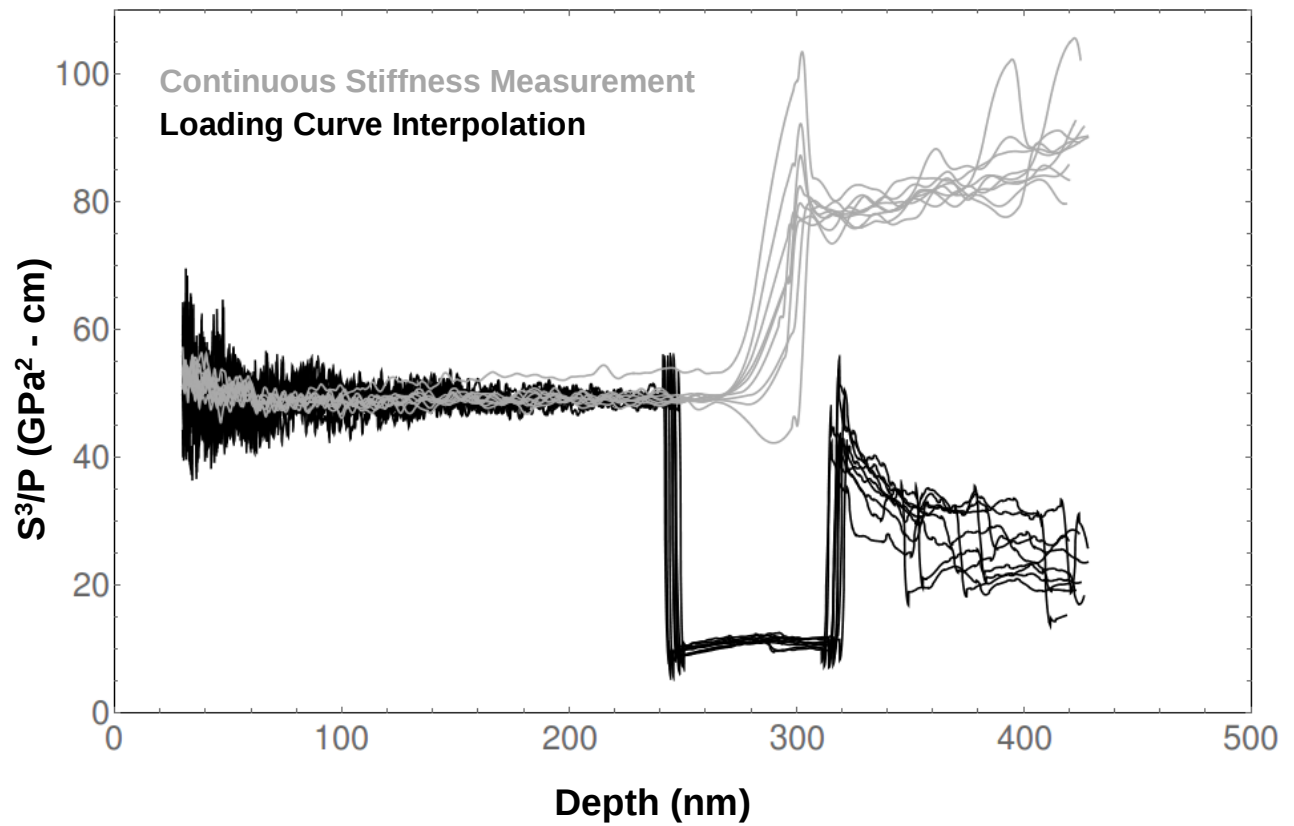


Figure 3.18: S^3/P spherical indentation versus depth of indenter displacement for Vit 106a BMG using an 8.6 μm radius tip. Two means of obtaining stiffness are showcased, and their divergence indicates the initiation of plasticity at the pop-in depth. The spike downwards of the interpolated loading stiffness curve (black) is an artifact discontinuous jump in displacement and the interpolation process.

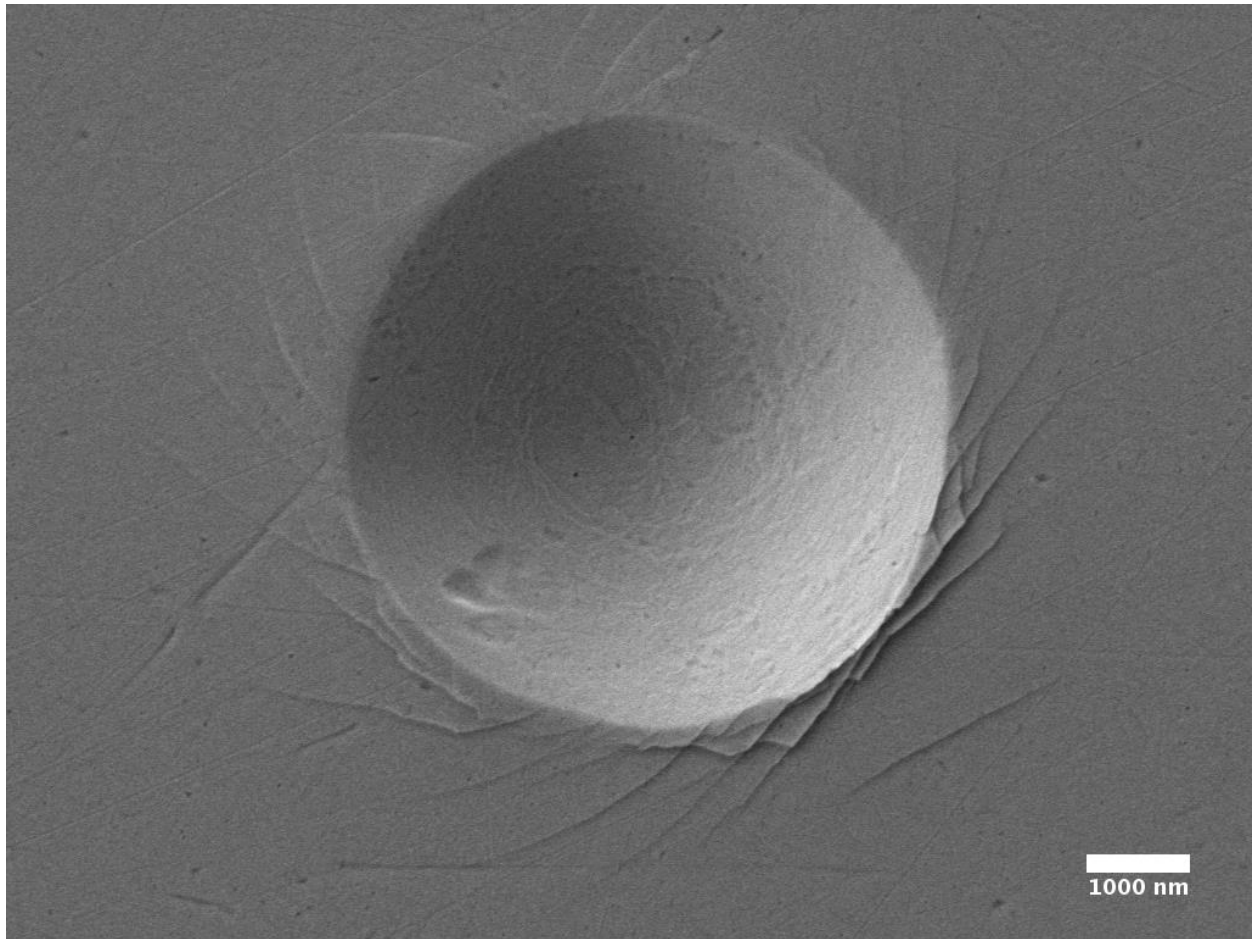


Figure 3.19: SEM micrograph of a 100 mN spherical indent on Vit. 106a BMG using an 8.6 μm radius round diamond tip. Multiple shear bands are seen accommodating plastic flow.

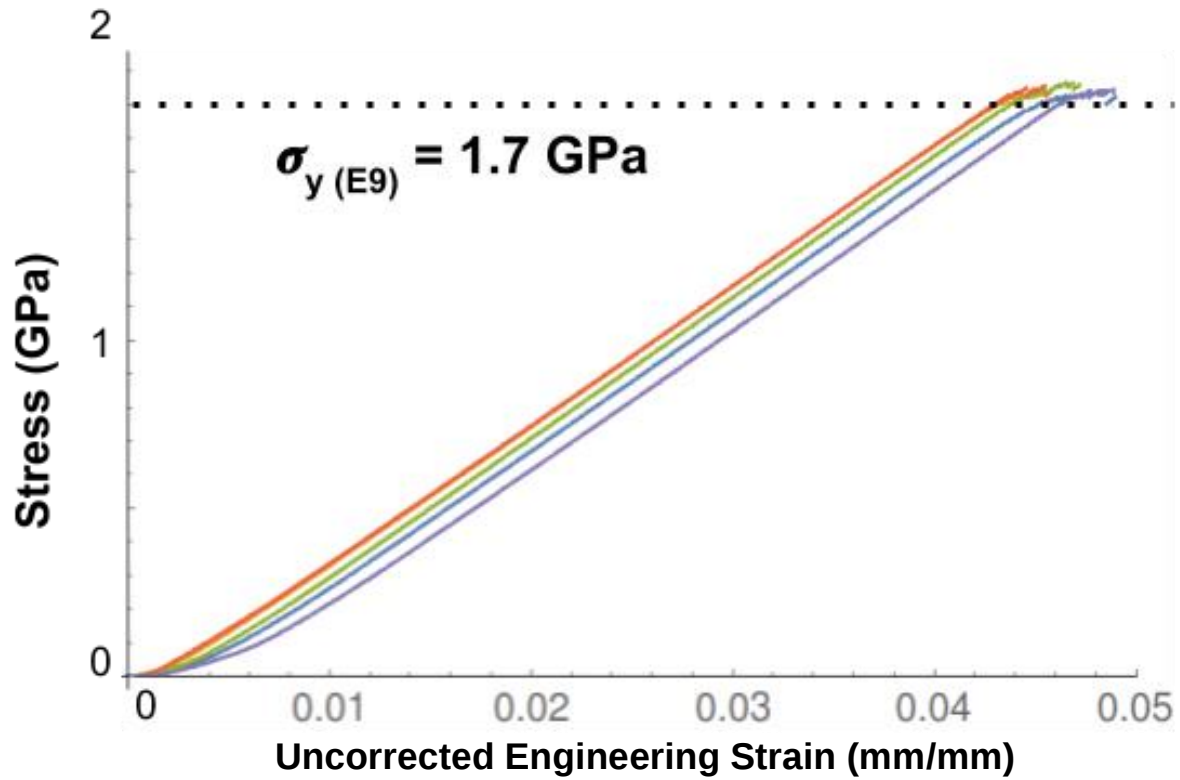


Figure 3.20: Compressive uniaxial loading of Vit 106a. Stress versus an uncorrected strain is displayed along with a horizontal dotted line marking the first discernable deviation away from linearity, the elastic limit, which is taken to be the yield stress.

design, often invalidates homogenous assumptions revealing microstructure-related mechanical property and/or size-dependent deformation mechanism differences. Commonly in glasses, homogeneity exists even down at the scale of nanoindentation. The yield stress determined for inorganic glasses therefore still holds validity as a bulk continuum property. For other materials, this assumption of homogeneity at the dimensional scale of the indentation contact may not be true. For instance, applying the methodology to BMG produced a large overestimation of the yield stress because of localization of deformation into shear bands which control small scale deformation processes.

Similarly, for electro-polished tungsten where dislocation sources are lacking [93], a localized plastic event resulted in gross overestimation of the yield stress at nearly 15x difference compared to the compressive yield value of a machined polycrystalline sample, which is closer to 550 MPa. It can be gathered that the mean contact pressure at which a pop-in event occurs is not equatable to an estimation of the bulk yield stress. It is further implied that the occurrence of pop-in events during the course of indentation are indicative of a breakdown of classical continuum descriptions of mechanics correspondent with scale of the indentation itself. Load displacement data for electro-polished and mechanically polished tungsten are displayed in Fig. 3.21 and Fig 3.22 respectively. If pop-in is observed in the load-displacement data, bulk property relatable yield stress values derived from the technique outlined in this chapter would be invalid.

Mechanically polished tungsten removed the discrete plastic events that led to distinct pop-in behavior by increasing the dislocation density. A separate issue arose regarding the lower limit of detection for transition from elastic to plastic deformation. The elastic modulus of the tungsten was too high (~400 GPa), which drove the yield point down to inaccessibly low depths. The yield point would be surpassed at just a depth of 5 nm for the 8.6 μm radius indenter. According to Fig. 3.8, the 500 μm radius indenter may have been able to capture the

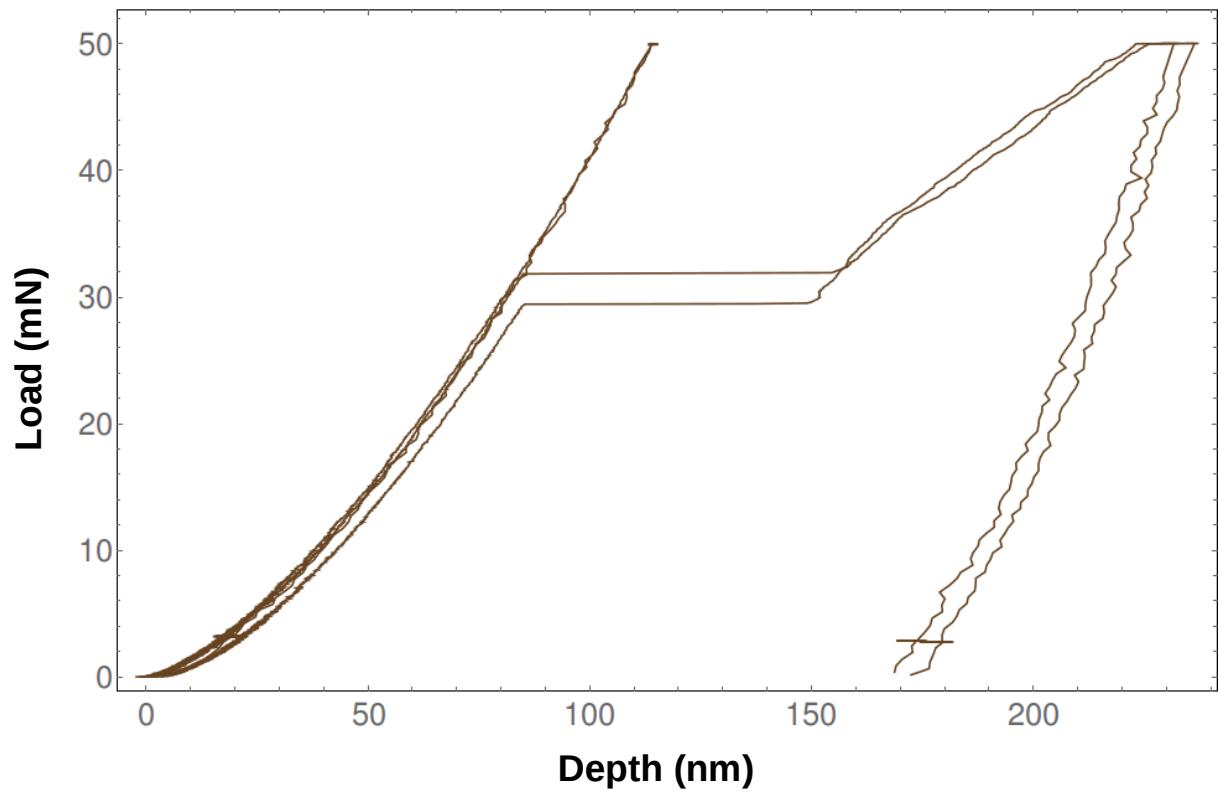


Figure 3.21: Three 50 mN and 8.6 μm radius spherical indentation load-indenter depth of penetration curves of electro-polished tungsten. Pop-ins are present in two of the three.

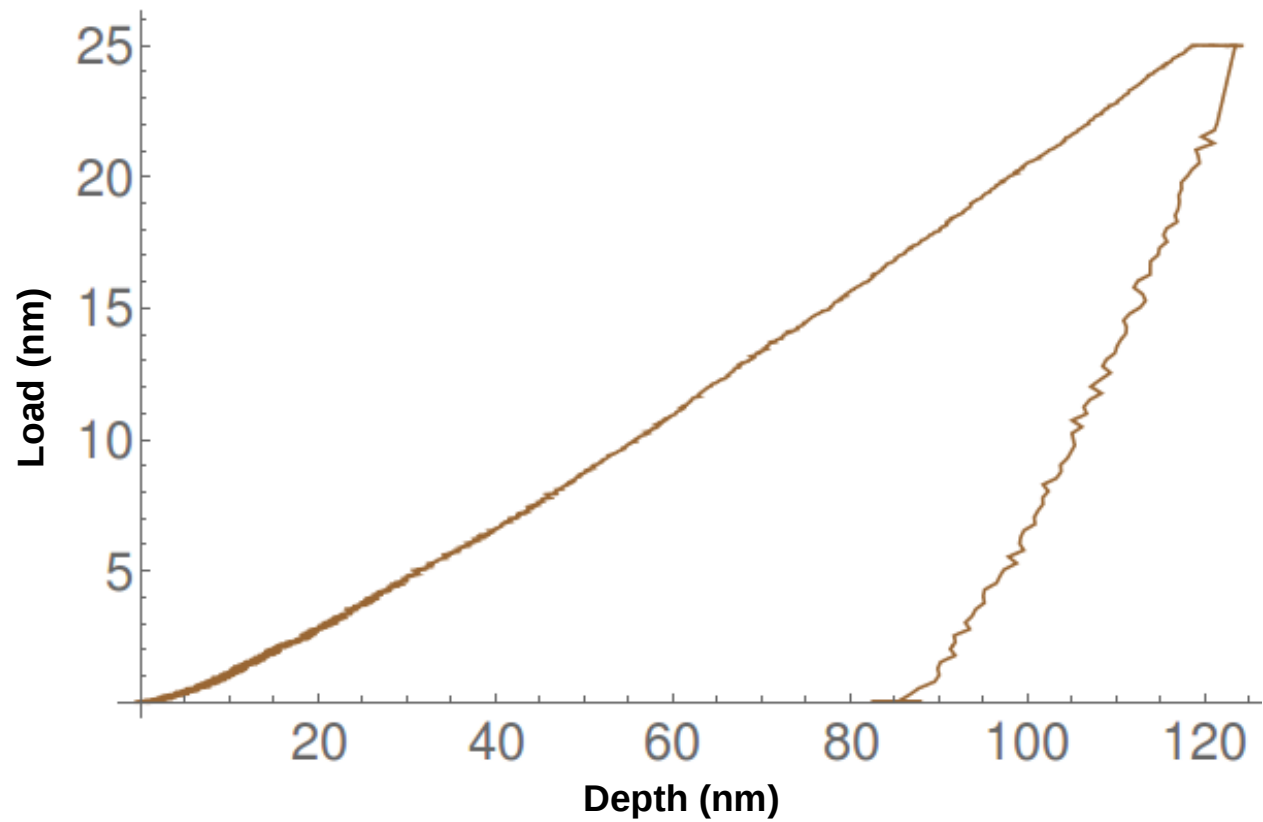


Figure 3.22: A 25 mN load-indenter depth of penetration curve of mechanically-polished tungsten. No pop-ins are present, but given the high elastic modulus of tungsten, neither the 8.6 μm , nor the 3.2 μm could resolve the elastic-plastic transition, which occurs at a depth level too shallow to detect.

yield point at a reasonable depth if perhaps the tungsten was hardened, but an intervening factor is that the large size of the indenter necessitated the use of sapphire as the indentation tip material. The risk of potential damage to the sapphire was deemed too great for its utilization on tungsten.

Titanium compression

The BMG sample provided an illustrative example for the breakdown of continuum assumptions, but what it did not provide was a valid test of the veracity of the overall method to determine the yield stress using spherical indentation. Titanium was turned to link the yield stress measured through spherical indentation and yield stress measured by uniaxial compression testing. The titanium was not annealed and was in an as-drawn state. The reasoning behind this was to leave little chance for a condition of low dislocation density to introduce heterogeneities witnessed with the electro-polished tungsten sample. The compressive stress curves are shown in Fig. 3.23a. There is significant machine compliance and slack that is initially present, but this again is inconsequential to the determination of the stress at which there is deviation from the linear elastic deformation regime. Fig. 3.23b singles out one of the tests and illustrates the yield stress of 380 MPa, which was consistent across the rest of the tests.

Plasticity did develop from a peak 750 mN load applied with a 500 μm radius spherical indenter as evidenced by the hysteresis of the load-indenter depth of penetration curve shown in Fig. 3.24. The stiffness cubed over load parameter for titanium indented with the 500 μm radius of curvature indenter is displayed in Fig. 3.25. The separation point is distinct and translates to a yield stress of 430 ± 30 MPa. This compares favorably to the yield stress obtained conventionally, albeit with some slight overestimation. Some overestimation is expected in part due to deformation occurring beneath the surface being a lagging indicator coupled with premature zero-point force surface acquisition, which is further exacerbated by the large contact

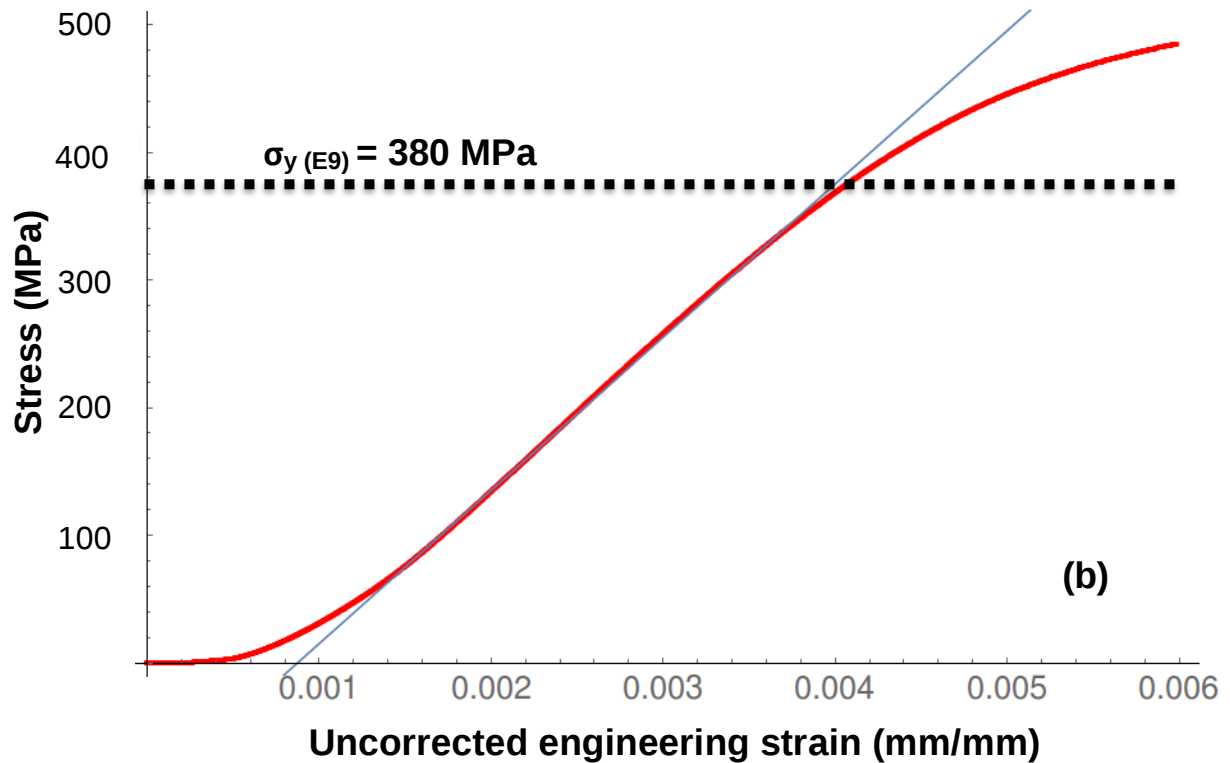
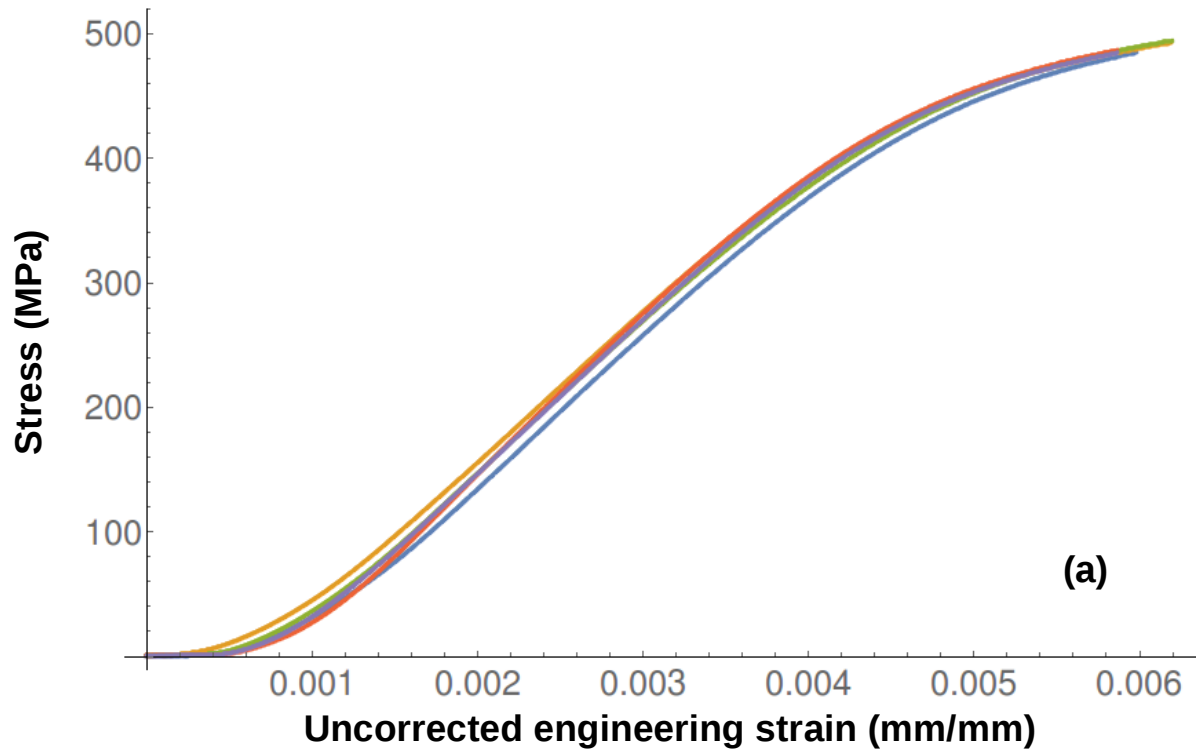


Figure 3.23: (a). Five successive uniaxial compressive tests of as-drawn high purity polycrystalline titanium rods. (b). A single test pulled from (a) shows the deviation from elastic linearity occurring at a stress of 380 MPa.

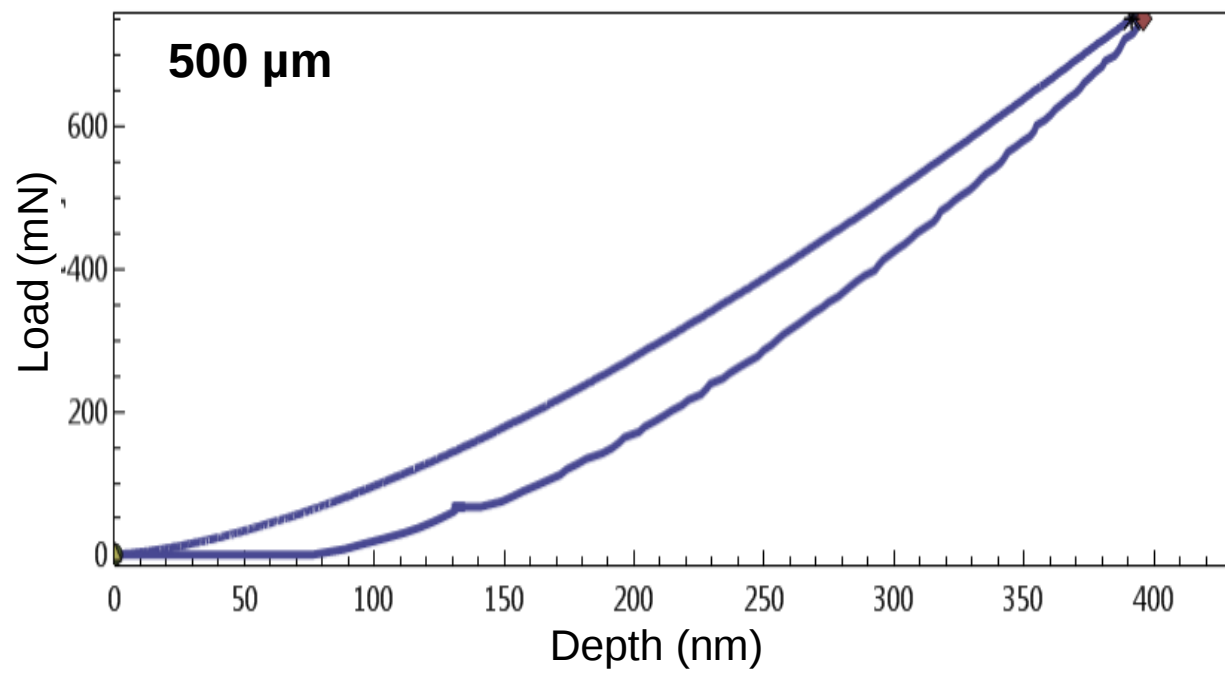


Figure 3.24: 750 mN peak load and 500 μm radius spherical indentation load versus indentation depth curve of titanium. Hysteresis is present, and there are no pop-ins.

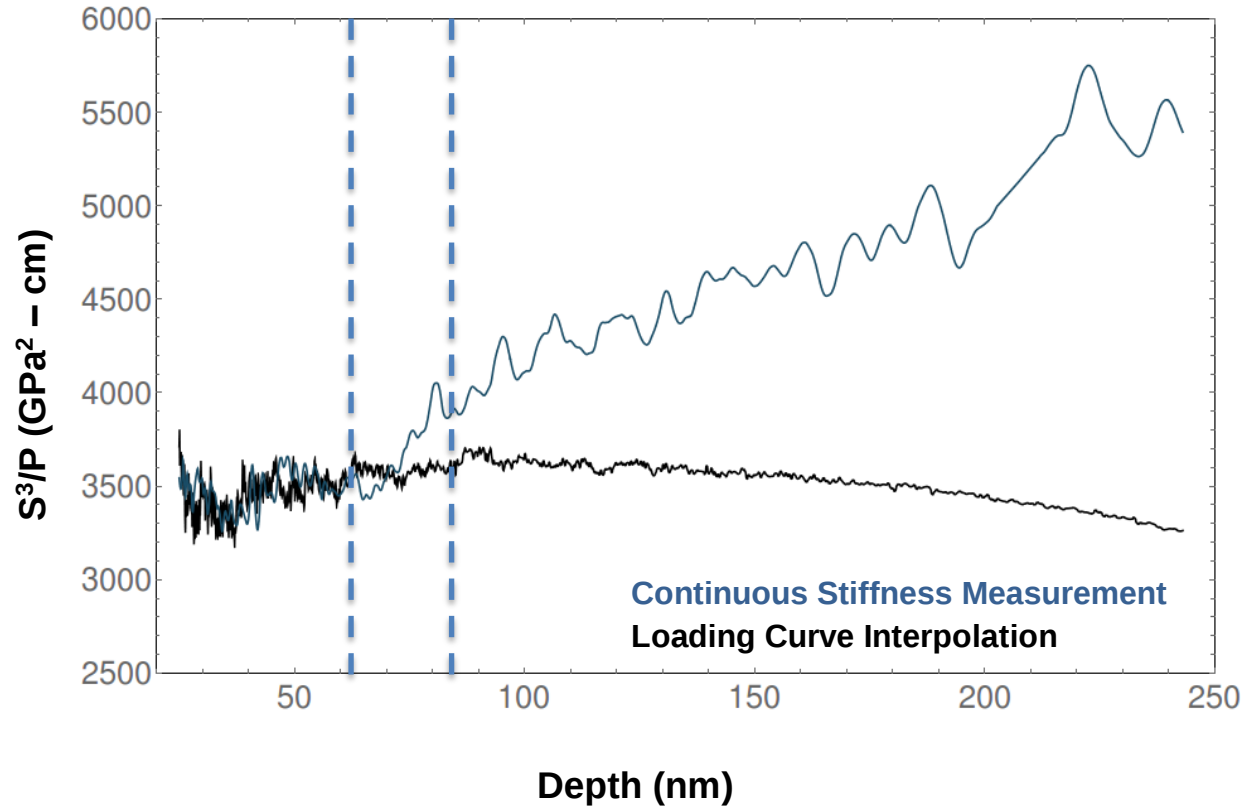


Figure 3.25: S^3/P versus indentation depth of penetration for a 500 μm radius sapphire sphere indenting a titanium sample. Divergence indicates yielding. ± 10 nm subjective uncertainty boundaries are vertically dashed on either side of the divergence point. The change in S^3/P is more pronounced for the dynamically-sourced continuous stiffness.

area to contact depth aspect ratio. The large aspect ratio is more sensitive to surface roughness artifacts, triggering surface detection too early. The important takeaway here is that the once deformation could be subsumed under continuum mechanics descriptions (through the use of as-drawn titanium and a large tip radius), the yield stress obtained by spherical indentation could be compared to bulk uniaxial compression. The veracity of the yield stress values determined using the divergence of the S^3/P parameter was established. Not only was the value obtained similar (13% relative difference), but also the slight overestimation can be assigned to known likely causes.

Conclusions

A new technique to determine the elastic limit and analogous yield stress of brittle materials using load and depth sensing spherical indentation was developed and evaluated. It is based on the development and interpretation of the instantaneous cube of contact-stiffness divided by the load (S^3/P). The method was applied to prototypical examples of normal and anomalous glasses: soda-lime silica and fused silica. The uncertainty of the method with regard to estimating the onset of yielding on a single test basis is superior to other spherical indentation methods.

The veracity of the method could not be confirmed using a bulk metallic glass or tungsten in part because the maximum shear stress criterion does not properly account for localized plastic flow. The accuracy of the method was corroborated using uniaxial compression testing high purity polycrystalline titanium samples machined from as-drawn rods. Since no pop-in was present for either fused silica or the soda-lime silicate, the maximum shear stress criterion provides a reasonable basis for estimation of the yield stress. Choosing or developing yielding criteria that contain components carrying physical significance to characteristics of experimentally observed mechanical responses is paramount in achieving accurate quantitative descriptions and predictors of mechanical behavior. Continued refinements to the method

should be possible through enhancement of experimental parameters to increase the dynamic signal to noise ratio, particularly at low depths. This newly developed method has enabled yield stress determination sourced from fundamental instrumented indentation measured quantities: force and displacement.

CHAPTER IV: EFFECTS OF THE PRESENCE OF WATER DURING SAMPLE SURFACE PREPARATION ON THE MEASUREMENT OF NANOMECHANICAL PROPERTIES OF BOROSILICATE GLASSES

Portions of this chapter have been published in Hackett, Benjamin L., Andrew A. Wereszczak, and George M. Pharr. "Effect of aqueous-based mechanical polishing on the nanoindentation response of borosilicate glasses." *International Journal of Applied Glass Science*, 10 (2019): 302-306.

Before the methodology developed in Chapter III can be properly applied to compositionally controlled borosilicate glasses, the surfaces of the glasses must be prepared for indentation through a process of planarization. In this chapter it is explored whether the presence of water during preparation of the surface of certain borosilicate glasses for indentation alters near-surface mechanical properties. The main message is to inform practical mindfulness of the potential detriment water associated with the surface planarization procedure has on accurate measurement of bulk material mechanical properties via indentation. The specific details of the grinding and polishing procedures are disclosed. The borosilicate glasses with the highest (BS15.7) and lowest borate (BS7.5) concentration were compared specifically to assess the influence of relative borate concentration on susceptibility to the effects of hydration during polishing.

When attempting to measure material properties by sampling near-surface volumes with techniques like nanoindentation, careful consideration of the state of the surface compared to the bulk is paramount for valid characterization. The process of surface planarization of glass in preparation for analysis is no exception. Water's general reactivity with silicate glasses has been well-established, but under the typical conditions for mechanical polishing, the usual practical assumption is that the potential effects on measured mechanical properties are insignificant due to the short period of glass-water interaction and the non-extreme corrosive environment. On the contrary, in this chapter it is shown that the act of polishing certain borosilicate glass compositions in an aqueous environment directly affects the nano-mechanical response to depths of several micrometers, reducing the measured elastic modulus and hardness by ~20% and ~35% respectively. Fourier transform infrared (FTIR) spectroscopy and

scanning electron microscopy (SEM) are used to confirm the formation of an altered, hydrated surface layer.

Glass Hydration Overview

Glass surfaces are not immune to chemical attack by water. The interaction of water and glass compositions has engendered numerous studies. The precise mechanism of reaction has been shown to be dependent upon the structure and corresponding composition of the glasses involved [94-97]. Water interaction with glass has been shown to alter many of its material properties and parameters such as density, index of refraction, thermal expansion coefficient, elastic modulus, hardness, and crack initiation threshold [98-102]. Consequently, knowledge of the effect of glass-water interaction is necessary to identify and optimize glass durability in the presence of water.

The composition, processing, and resulting glass network structure determine glass dissolution response [103]. The predominant silicate glass-water interactions include penetration of molecular water into the surface (hydration), formation of hydroxyl groups (hydrolysis), and cation exchange [97]. A destructive consequence of these interactions is selective dissolution, in which the more soluble components of a silicate glass are preferentially dissociated [104]. Borosilicate glasses can be susceptible to this influence of water even though many borosilicate compositions are used chiefly because of their high chemical durability [105].

While many studies have focused on the molecular mechanisms at the basis of the glass-water interaction, less attention has been directed towards the potential practical significance of surface preparation involving water and subsequent measurement of mechanical properties via nanoindentation. In this study, the effect of mechanically polishing two borosilicate glasses in an aqueous polishing environment on the near-surface mechanical properties and structure is investigated using nanoindentation, FTIR spectroscopy, and SEM observation of the surface.

Experimental Procedure

Materials

Two borosilicate glass compositions were tested and are designated as BS7.5 and BS15.7. The compositions are labeled BSX, where the label X refers to the molar percentage of borate. The molar compositions and molar ratios K ($\text{SiO}_2/\text{B}_2\text{O}_3$) and R ($\text{Na}_2\text{O}/\text{B}_2\text{O}_3$) for the glasses are listed in Table 2.1 and Table 2.2.

Surface preparation

Two discrete surface preparation procedures were followed: one in which water was acceptable to use, and the other where it was not. For the aqueous method, water was used to rinse and clean the sample between each grinding and polishing step, whereas ethyl alcohol was used instead for the non-aqueous method. Initial coarse grinding used 800 and 1200 grit SiC grinding paper for each. A fine polish was achieved by both methods using progressively finer diamond suspensions (6, 3, 1, and 0.5 μm) on polishing discs and cloths. The lapping lubricants differed between the two methods. An oil-based lubricant (Engis HYPREZ® OS Type IV) was used for the non-aqueous method, and an alcohol-based lubricant (Struers DP-Lubricant Purple) was used for the aqueous method. Each glass sample was ground for 2 minutes and polished for 50 minutes total with seven combined grinding and polishing steps. The two polishing methods described, when applied to both the BS7.5 and BS15.7 glasses, produced four distinct specimens (20 mm x 20 mm x 3 mm). After grinding and polishing was complete, samples were wiped clean with acetone.

FTIR

Structural bonding resonance information from each glass surface was obtained with a FTIR spectrometer (Thermo Scientific, Nicolet iS50, Waltham, MA) at the same room temperature and ambient humidity. An attenuated total reflectance (ATR) cell was used to acquire spectra over a range of 600 - 4000 cm^{-1} .

Nanoindentation

Nanoindentation was performed on all four glass samples at ambient conditions. A commercial nanoindenter (Nanomechanics, iMicro Nanoindenter, Oak Ridge, TN) was used to generate 9 indents in a 3 x 3 array for each sample with a maximum test load of 400 mN for each indent. All tests were carried out with a constant loading rate to load ratio ($\dot{P}/P$) of 0.2 s^{-1} . Poisson ratios were independently obtained from resonant ultrasound spectroscopy (RUS) measurements and are included in Table 2.2. The indenter tip material was diamond, and the tip geometry was Berkovich (a three-sided pyramid with 65.3° face to centerline angle). Continuous stiffness measurement, whereby oscillatory load-unload harmonics overlay the general application of load (P), was used in order to evaluate measures of hardness (H) and elastic modulus (E) as a function of indenter penetration depth (h) according to the Oliver-Pharr method [53]. The expression for the elastic modulus of the target material is

$$E = \frac{(1-\nu^2)}{\left(\frac{\left(\frac{2\sqrt{A}}{S\sqrt{\pi}} \right) - (1-\nu_i^2)}{E_i} \right)} \quad (4.1)$$

where S is the stiffness, A is the contact area, ν is Poisson's ratio, and the subscript i represents the diamond indenter elastic properties ($E_i = 1140 \text{ GPa}$, $\nu_i = 0.07$).

Electron microscopy

A field-emission scanning electron microscope (Zeiss Auriga, Carl Zeiss Microscopy, Jena, Germany) at an accelerating voltage of 1 kV was used to view the indents and fine surface details.

Results and Discussion

Elastic modulus and hardness

A comparison between the nanomechanical responses of the two different polishing environments and the two borosilicate glass compositions was made. Comparing first with just the load-displacement curve in Fig. 4.1, the aqueously polished BS15.7 sample deforms to a greater depth than the oil-polished BS15.7 for the same peak load of 400 mN. Elastic moduli for the two glass pairs are plotted as a function of indenter penetration depth in Fig. 4.2. The elastic modulus of the aqueously-polished BS15.7 at low penetration depths is ~ 20% lower than oil-polished BS15.7. As penetration depth increases, the aqueously-polished curve converges to the oil-polished curve. Oil-polished BS15.7 exhibits an invariant elastic modulus with indent depth, disbaring the changes potentially associated with tip rounding defects at depths less than 100 nm. Aqueously polished BS7.5 exhibited no significant elastic modulus differences compared to its oil-polished correlative. The acquired elastic moduli data constitute a probed volume beneath the contact. The dynamic nature of the elastic modulus of aqueously-polished BS15.7 mirrors that of thin films in circumstances where there is a compliant film atop a stiffer substrate [98,106]. If the thickness of the film is small compared to the depth of the indent, the volume of material probed will include both the film and the substrate. The measured elastic modulus will then be a combination of the film and substrate elastic moduli. In the present case, the source of the compliant film-like behavior arises from differences in surface preparation procedures, namely that polishing in the presence of water alters the surface forming a hydrated surface layer with lower elastic modulus than the unaffected bulk glass “substrate”. Since the elastic modulus converges to a stable value of 57.7 GPa as indent depth is increased, an upper limit may be placed on the hydrated layer thickness at the point of convergence marking the influence of the modified surface becomes negligible. Here, the estimated maximum layer thickness is 1.5 μm .

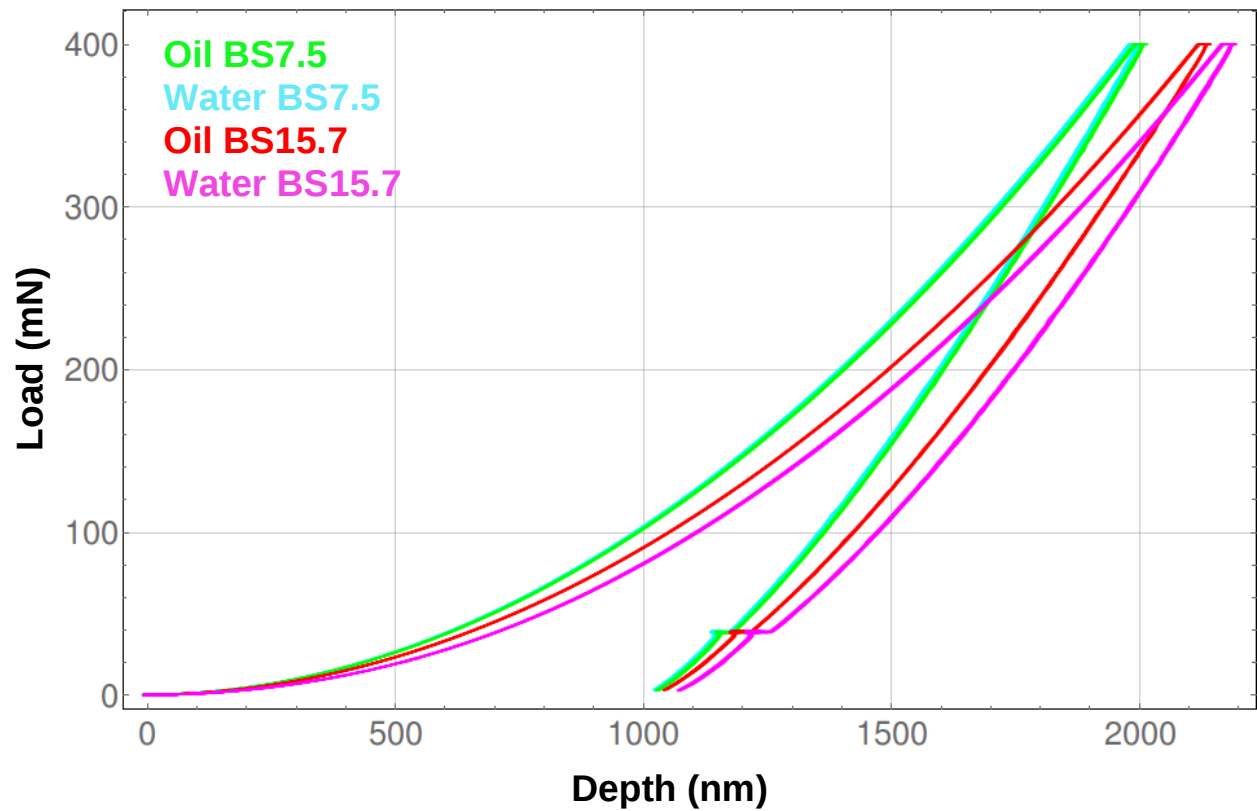


Figure 4.1: Load-displacement curves for the two pairs of samples. The water-polished BS7.5 is nearly indistinguishable from the oil-polished BS7.5. Conversely, the water polished BS15.7 deforms to a greater depth at the same peak load of 400 mN.

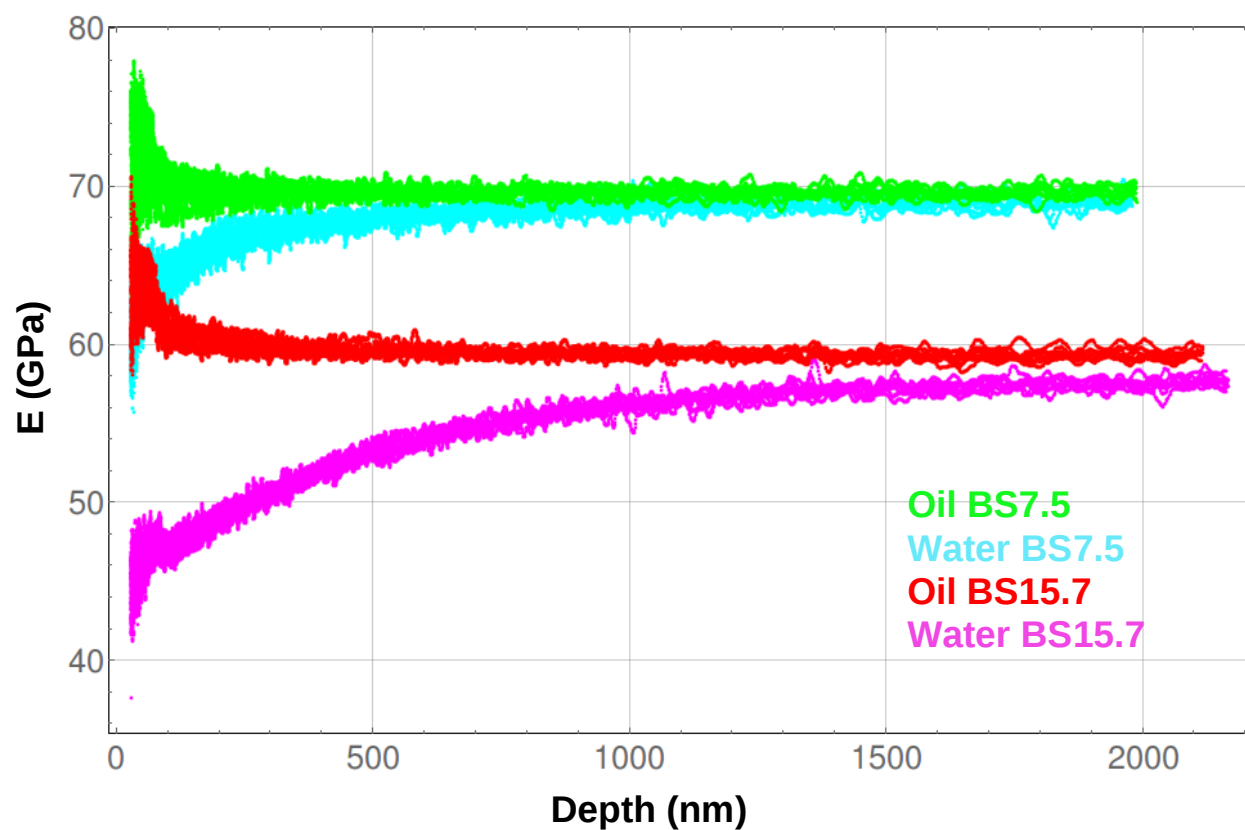


Figure 4.2: The elastic modulus plotted as a function of depth for the pairs of samples. At depths below 1500 nm, the water-polished BS15.7 shows much lower elastic modulus than its oil-polished counterparts. A similar but smaller effect is seen for the BS7.5 pair.

Hardness is defined as

$$H = P/A \quad (4.2)$$

and describes the resistance of a material to plastic deformation. In contrast to elastic modulus, hardness is not considered to be a material property because of its dependence on the indenter geometry and indenter material. Nevertheless, hardness provides a useful comparative element of deformation information localized to the contact surface, stemming from its relation to contact area. Hardness of the glasses versus indenter depth is shown in Fig. 4.3. The hardness of the aqueous-polished BS15.7 is ~ 35% lower than the oil-polished BS15.7 at low indenter depths (< 250 nm) and ~ 10% lower at the maximum depth of penetration. As with elastic modulus, the hardness also increases with indent depth, but unlike the elastic modulus, the hardness of aqueously-polished BS15.7 does not asymptotically approach the hardness of oil-polished BS15.7 over the depth range that could be probed (approximately 2000 nm). At the maximum depth of penetration, the difference in hardness is ~ 1 GPa. There is no close convergence within the range probed due to the surface-localized scope of the hardness. The nanoindentation-derived hardness for the aqueously polished BS7.5 is ~ 2% lower than the oil-polished BS7.5.

Porosity

Porosity may develop as a consequence of selective leaching during dissolution [97]. A low chemically durable borate rich phase may be leached away by reactions with water leaving behind a porous and gel-like silica-rich superstructure [107,108]. A porous structure, exhibited in Fig. 4.4a., is present on the surface of aqueously-polished BS15.7. The approximate diameter of the pores is 20 nm. As shown in Fig. 4.4b, no evidence of similar porosity was recognized for the oil-polished BS15.7. The lower hardness and elastic modulus at shallow indenter depths

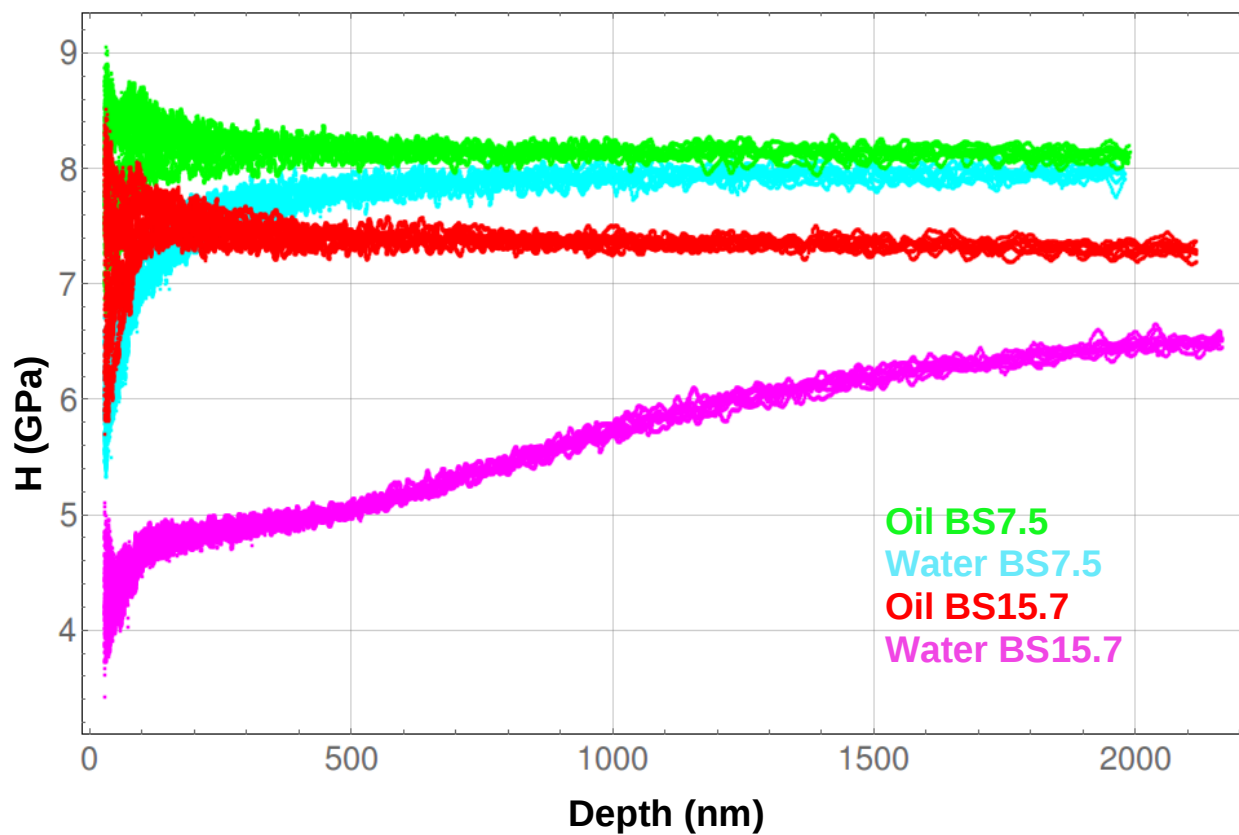


Figure 4.3: Berkovich indentation hardness as a function of indenter penetration depth.

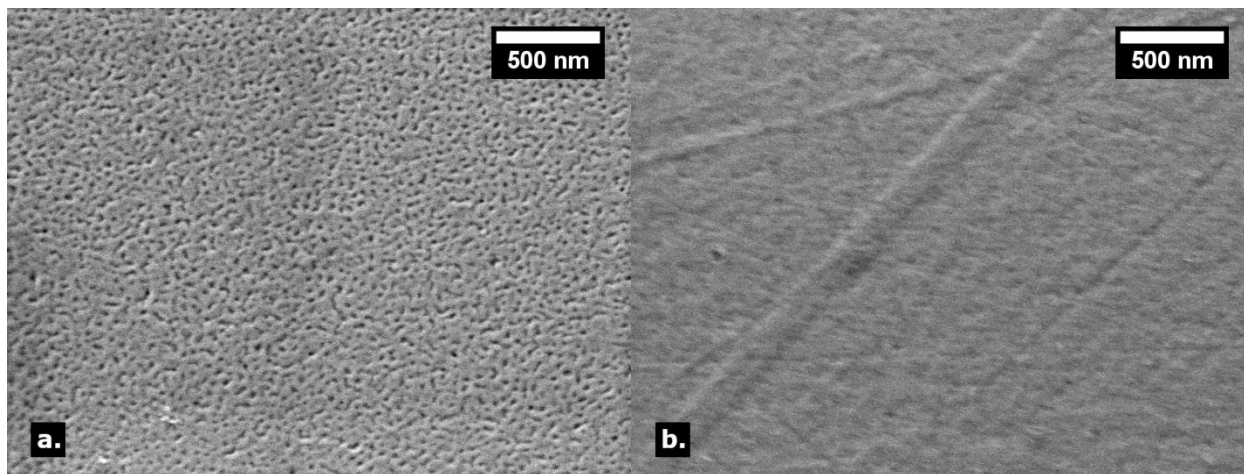


Figure 4.4: SEM micrographs comparing (a). aqueously-polished and (b). oil-polished surfaces. Porosity appears more prominent and widespread in (a). Some residual polishing marks are visible in (b).

compared to the maximum depth of penetration for BS15.7 can thus be attributed in part to its leached porous surface structure because of the aqueous mechanical polishing. BS7.5 did not exhibit porosity resolvable by SEM. Phase separation may be the underlying reason for differences in localized leaching rates that lead to the development of the observed fine porous structure.

FTIR spectra and borosilicate-water interaction

The FTIR spectra in Fig. 4.5, scaled relative to the most intense peak, compare the infrared absorbance of aqueous to oil-polished borosilicates. The broad absorption band centered between the range of 3225 to 3450 cm^{-1} , which is assigned to bending overtones and symmetric and asymmetric stretching of H_2O , indicates the presence molecular water [109-111]. The H_2O -specific lower wavenumbers within the overall band are the unique dominating spectral features associated with the glasses polished in the aqueous environment. Signatures of OH stretching in Si-OH, Si-OH hydrogen bonded to the oxygen of a neighboring Si-OH, and Si-OH hydrogen bonded with non-bridging oxygens are also observed with absorption features located at 3600, 3510, and 2900 cm^{-1} respectively [109-111]. Fig. 4.6 compares just the BS15.7 pair and confirms the presence of molecular water with its characteristic bending vibration at 1630 cm^{-1} . The oil-polished BS15.7 showed no trace of that band. A stronger absorption signal was observed for aqueously-polished BS15.7. The elevated absorption reveals an increased degree of reaction and uptake of water in the surface along with changes in the molecular and network structure of the glass. Dual sharp peaks at 2855 and 2920 cm^{-1} suggest that some hydrocarbon contamination may have potentially resulted from insufficient cleaning of fingerprints or lubricant residue. Nevertheless, especially for BS15.7, aqueous mechanical polishing according to the experimental procedure did introduce identifiable surface hydration effects, ultimately altering the surface mechanical properties relative to the oil-based polishing procedure. That relatively brief exposure to water during the process of mechanical polishing could lead to measurable

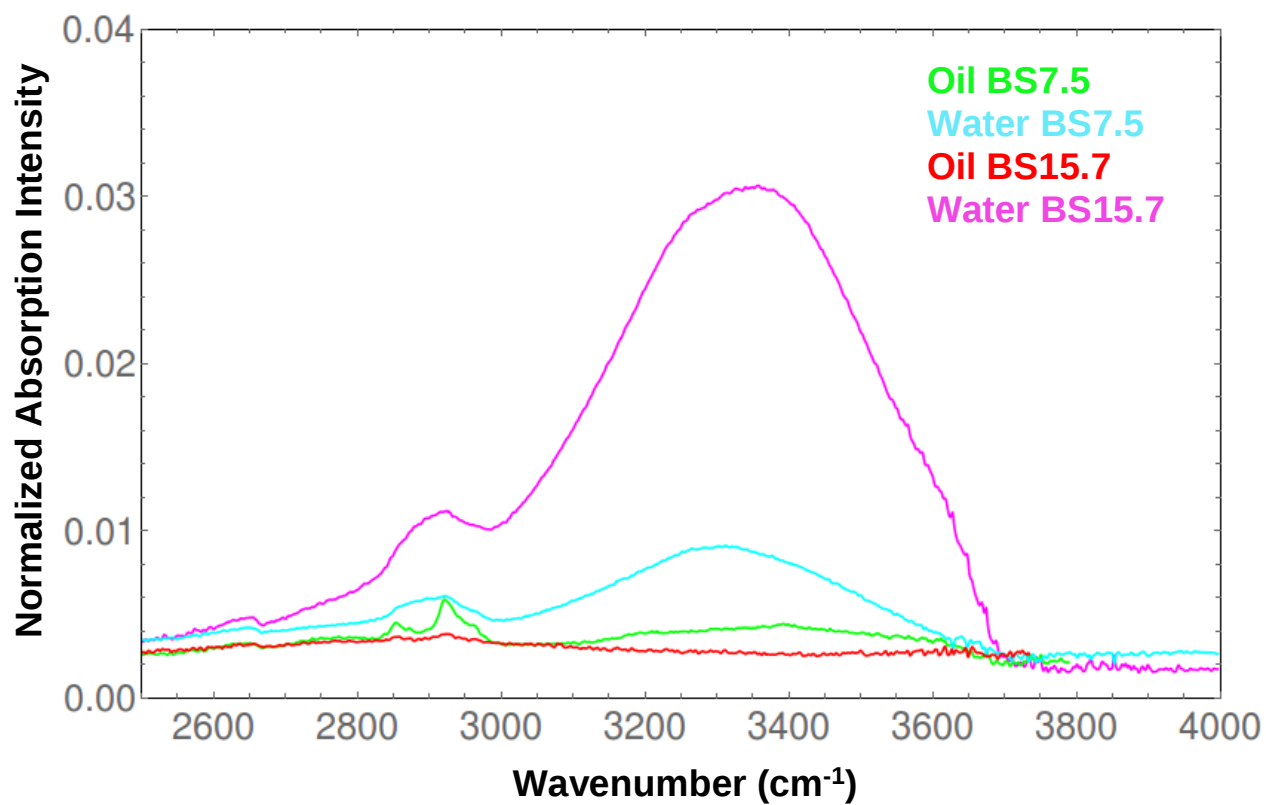


Figure 4.5: FTIR absorbance spectra of the four borosilicate glass samples.

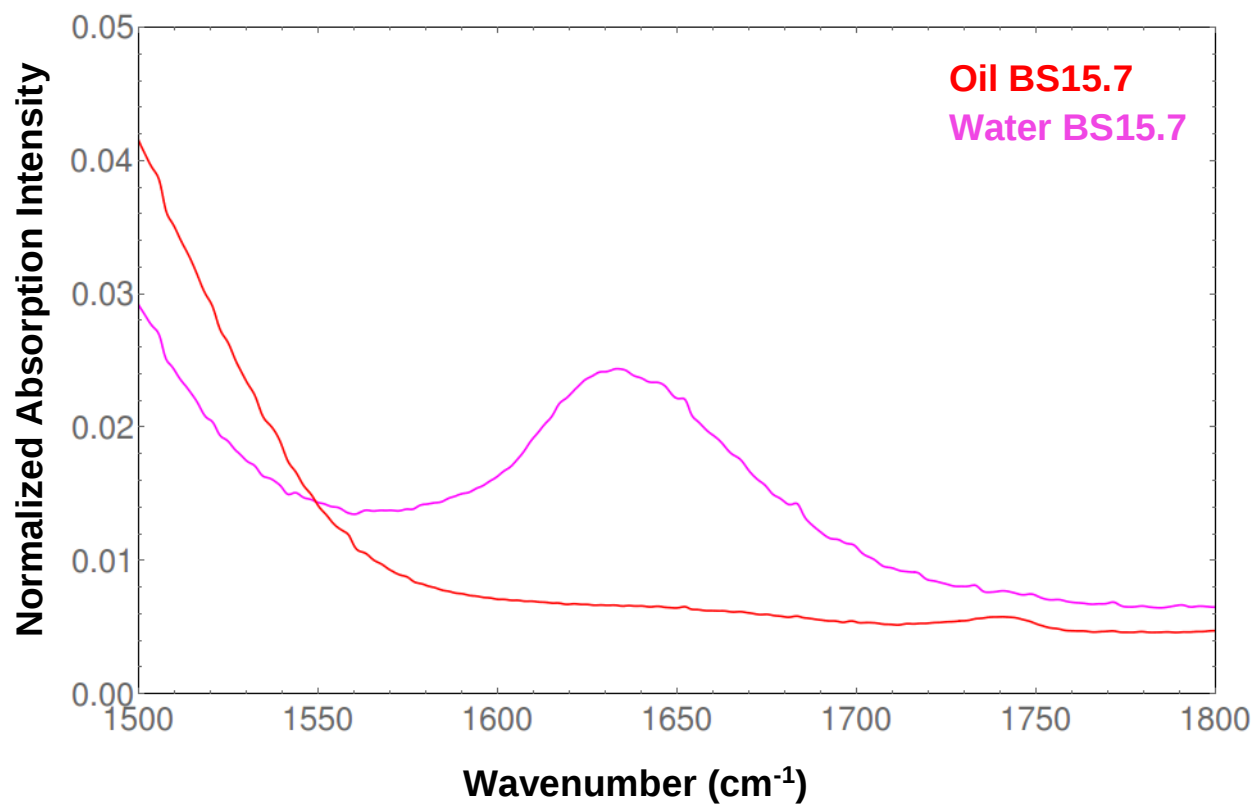
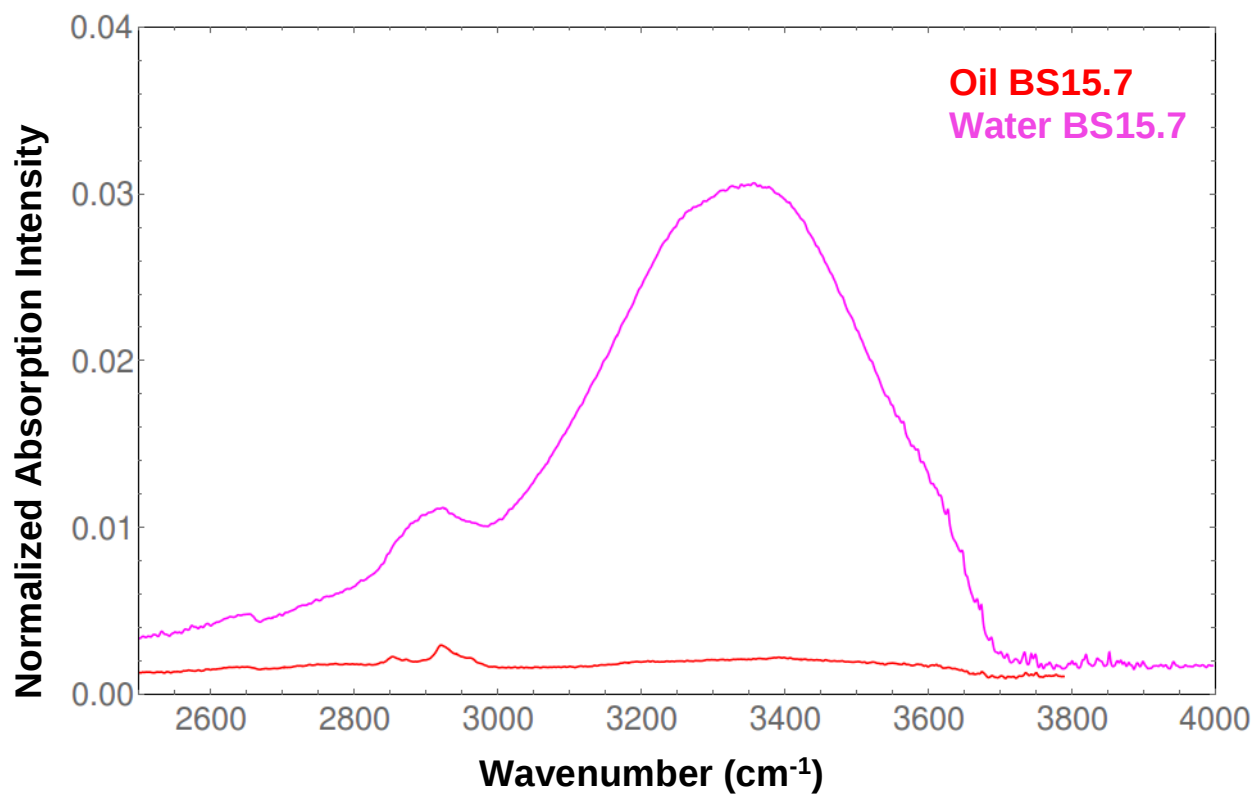


Figure 4.6: Two segments of the FTIR absorbance spectra focusing on vibrations attributed to the presence of water. Top: asymmetric OH stretching associated more strongly with H_2O
Bottom: characteristic bending vibrations of the H_2O molecule

mechanical property differences for these borosilicate compositions due to effects of hydration was unexpected. The glass was not exposed to the usual environmental conditions favoring corrosive action such as complete submersion in water for days [98], acidic attack [112], or elevated temperature and pressure encountered in an autoclave [113]. Yet, it could be reasoned that the mechanical action of polishing in an aqueous medium introduces comparable conditions and involves the same components: water, heating (frictional), and locally high pressure (from the grinding and polishing pads) [114].

Conclusions

The aqueous-based polishing of borosilicate glasses appears to have activated chemical and structural alteration in the BS15.7 borosilicate glass at shallow surface depths ($< 1.5 \mu\text{m}$). The water signatures within the FTIR spectra and observable nanoporous surface structure are consistent with this surface alteration effect. As a result of the formation of a porous and hydrated surface layer, both the elastic modulus and hardness, estimated using Berkovich nanoindentation, of aqueously polished BS15.7 were lower than the BS15.7 oil-polished variant at shallow depths characterized by the thickness of the affected surface layer. BS15.7, containing higher borate concentration than BS7.5, is more prone to surface alteration induced by aqueous-based mechanical polishing.

These results and observations demonstrate that in order to better preserve the surface-bulk integrity of the borosilicate glass compositions studied here, oil-based mechanical polishing is preferable to aqueous-based mechanical polishing. Aqueous-based polishing can introduce structural changes to the surface influencing the nanoindentation response and produces misleadingly low and non-representative measurement of hardness and elastic modulus characterizing the bulk material. Caution thus ought to be exercised with specimen preparation for nanoindentation of potentially water-susceptible borosilicates.

CHAPTER V: YIELD STRESS DETERMINATION AND STRUCTURAL RELATIONS TO THE HIGH- PRESSURE MECHANICAL RESPONSE OF BOROSILICATE GLASSES

The prior chapters have established the necessary preconditions for the studying the effect of varying the relative ratios of SiO_2 to B_2O_3 (network former substitution) in borosilicate glasses on the mechanical yielding response: a novel methodology for estimating the yield stress (Chapter III) and recognition of deleterious effects of water contact with the selected glass compositions during sample surface preparation (Chapter IV). Isolating the focus and analysis just to the potential differences in mechanical response without due consideration of the material structural basis for the differences would produce insights of shallow depth. Therefore, several supportive elements are added in this chapter placing the yielding response in a broader context.

The complete resulting dataset includes yield stress, indentation hardness, and elastic modulus along with density, Raman, and ATR-FTIR spectra for the three borosilicate glass compositions at baseline 0 GPa pressure and then incremented to a maximum hydrostatic pressure of approximately 12 GPa. The reason for the numerous additional factors is to supply wider context and draw from potential correlation to the yield stress values for each glass composition. This chapter is separated into two parts. The first analyzes the effect of network former substitution on the yield stress. The second section addresses the effect of hydrostatic pressure and associated densification on the yield stress of the three glasses.

Yield Stress and Composition

The yield stress of each of the three borosilicate glasses was estimated using the experimental technique developed in Chapter III. The championed technique gives an indication of deviation from perfectly elastic behavior through sensing relative radius of contact changes linked directly to the formation of a residual impression through analysis of the parameter S^3/P . Indentation was carried out at to peak load of 40 mN at a constant 0.2 s^{-1} loading rate to load ratio that is the indentation correlative of strain rate.

The conclusions reached in Chapter IV cautioned against the use of water in the surface preparation of the borosilicate glass compositions under study. An identical grinding and polishing procedure, which avoids water and uses lapping oil in its place, was followed for all three of the samples. Two diamond spheres with radii sizes of 3.2 μm and 8.6 μm were used to determine the yield stress. Using two different radii sizes would expose any strong size effect. The yield stress should be independent of the size of the radii if the deformation mechanics are the same and the material is homogeneous at the scale of the indentation impression size. Alongside spherical nanoindentation-derived yield stress, a diamond tip with a three-sided pyramidal base measured the indentation hardness and elastic modulus according to the Oliver-Pharr method [53]. The instrumented nanoindenter allows for stiffness to be continuously measured according to [84] achieving E and H as a function of indenter displacement.

Adding to the robustness of the data, the Young's modulus and Poisson ratio were measured by resonant frequency ultrasonic spectroscopy. Knowing the Poisson ratio helps to ensure that the proper measure of yield stress is made, since there is a slight Poisson ratio dependency of the conversion between mean contact pressure and yield stress.

Fig. 5.1 shows load versus displacement generated using the 3.2 μm radius for all three borosilicate compositions together. Nine tests each for a total of 27 are simultaneously plotted. The load displacement curves are highly repeatable. Distinct separation of the three compositions is observed, giving the first indication that the three compositions are at the very least deforming differently to the equally applied 40 mN peak load. For the same peak load, BS15.7 deformed the most, followed by BS11.1, and BS7.5 the least. BS7.5 and BS11.1 leave a similar residual contact depth after the load is completely removed.

The S^3/P versus indenter surface penetration depth plots using the 3.2 μm tip radius are shown for the three glass compositions in Fig. 5.2. The general form of the curves is similar for all three. The mostly flat and matching initial portion of the dual-sourced stiffness cubed

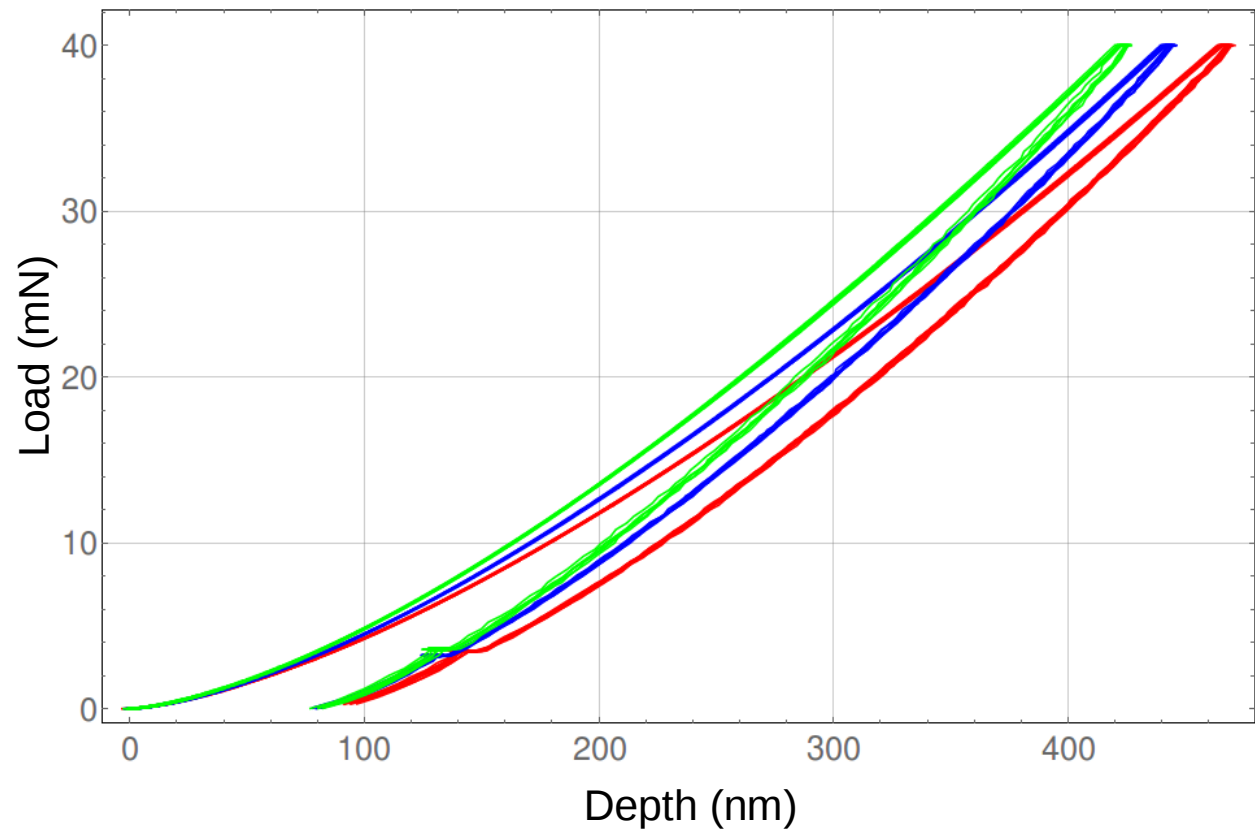


Figure 5.1: Load as a function of indentation depth for the three borosilicate glass compositions.

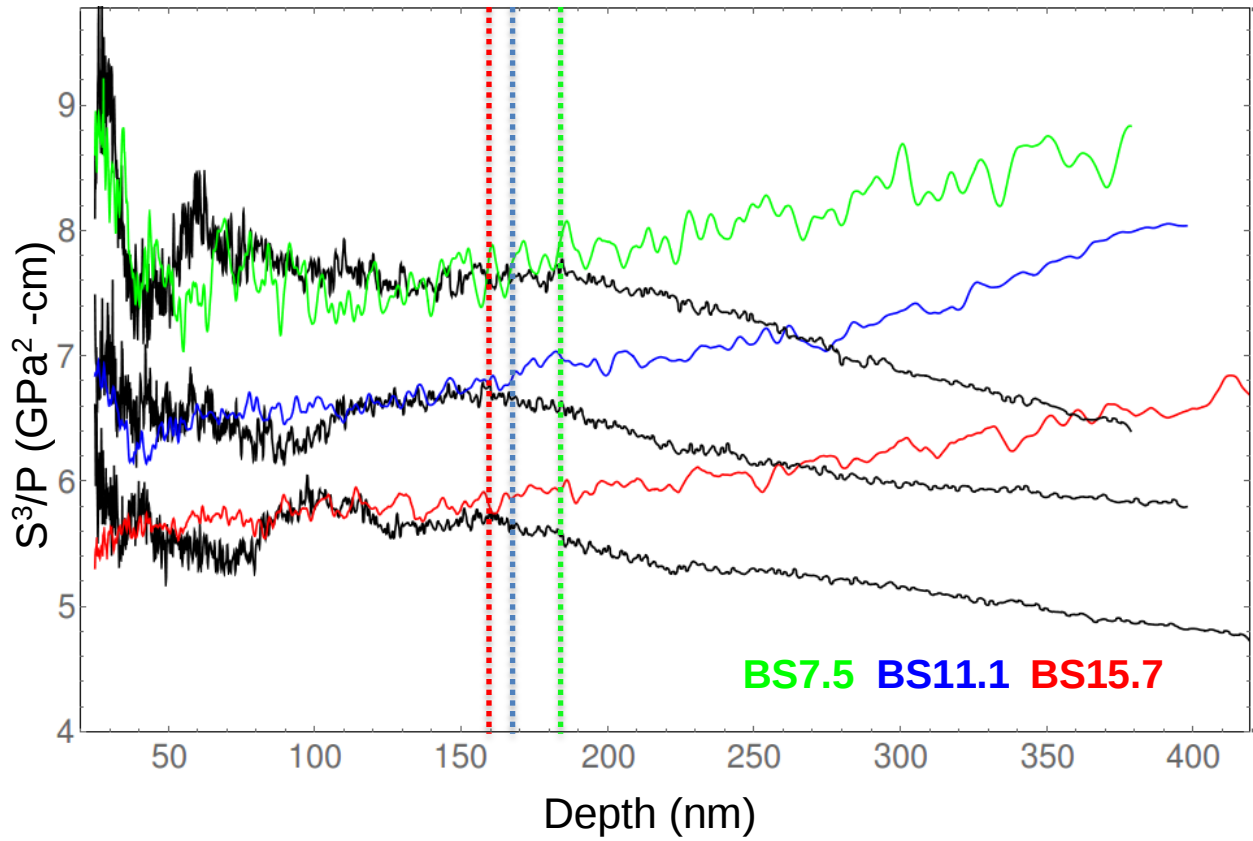


Figure 5.2: S^3/P indentation divergence curves for the three borosilicate glass compositions. The dotted vertical lines mark the divergence point for each glass. Colored curves indicate stiffness sourced from continuous dynamic measurement while the black curves indicate the interpolated loading curve stiffness source for each associated composition.

overload curves is in accordance with elastic spherical contact with fixed relative radii of curvature. Divergence of the dynamically sourced unloading and the interpolation-based loading stiffness occurs for each glass composition. Conversion of the critical depth of contact at the divergence to contact stresses is made. Once the principal stresses are determined, the maximum-shear stress yield criterion was chosen for a yield stress conversion. The yield stress values are given in Table 5.1. Even if the separation of curves were to occur at equivalent values of indenter penetration depth for all three, the differences in elastic moduli cause the contact stresses to be different in each case. The magnitude of the S^3/P parameter scales as the square of the reduced elastic modulus, all else equal. The fact that BS15.7 has the highest initial S^3/P value entails that BS15.7 also must have the highest elastic modulus out of the three glasses. This finding is supported by the complementary RUS measurements of the elastic properties of the glasses which are listed in Table 5.2.

The simple trend observed is that the yield stress increases with increases in the molar ratio of SiO_2 to B_2O_3 . Yield stress values obtained remained consistent across the two indenter sphere radii used. No size-dependency of the yield stress was observed between the two, but this doesn't completely discount the possibility that a size effect could be present and distinguishable over a more expansive range of spherical indenter sizes.

Berkovich nanoindentation provided additional mechanical information in the form of indentation hardness and elastic modulus which is also included in Table 5.2. The ratio of the hardness to the yield stress, the constraint factor, is listed too. The constraint factor has a negative correlation to K between the three glass compositions even though the general trends of elastic modulus, indentation hardness, and yield stress are all positively correlated to K . A constraint factor near three is emblematic of a material with fully developed (uncontained) plasticity. Thus, in having a higher constraint factor, a material has a greater relative plastic versus elastic deformation character. A higher relative constraint factor also implies that plastic

Table 5.1: Yield Stresses for Three Borosilicate Glasses Determined Using New Spherical Indentation Method

Glass Composition	σ_y (3.2 μm radius)	σ_y (8.6 μm radius)
BS7.5	6.6 ± 0.2 GPa	6.5 ± 0.1 GPa
BS11.1	5.8 ± 0.2 GPa	5.7 ± 0.1 GPa
BS15.7	5.3 ± 0.2 GPa	5.4 ± 0.1 GPa

Table 5.2. Mechanical Properties and Density of Pressurized Glasses

Glass Composition and Maximum Pressurization	σ_y (3.2 μm) ± 0.2 GPa	E (GPa)	H (GPa)	ρ (g/cm ³)	C (H/ σ_y)	E _{RUS} (GPa)	ν
<u>BS7.5</u> 0 GPa 2 GPa 4 GPa 8 GPa 12 GPa	6.6 6.6 6.5 6.7 7.3	68.4 67.5 68.9 77.1 80.7	7.4 7.4 7.3 7.4 7.9	2.20 2.22 2.24 2.29 2.44	1.12 1.12 1.12 1.10 1.07	67.6	0.17
<u>Borofloat</u> 0 GPa 12 GPa	5.7 6.1	63.7 73.5	6.9 7.3	2.19 2.44	1.21 1.18	63.1	0.18
<u>BS15.7</u> 0 GPa 12 GPa	5.3 5.9	57.9 70.2	6.7 7.1	2.16 2.37	1.26 1.22	57.6	0.205

deformation in that material is constrained relatively less by the effect of elastic confinement [115]. Yield stress, elastic modulus, and indentation hardness were all found to be positively correlated with the ratio of SiO_2 to B_2O_3 .

Structural characterization from FTIR spectroscopy

In order to reveal the potential structural differences among the presently studied glasses that could be caused by differences in composition and be at the root of the mechanical property differences, spectroscopic analysis was carried out using ATR-FTIR and Raman techniques. Producing FTIR spectra elicits information regarding the bond vibrations, which can then be assigned to specific bonding arrangement. In this manner, the short to medium range bonding is revealed. The FTIR spectra comparison of the three glasses is shown in Fig. 5.3 over the range 650 cm^{-1} to 1600 cm^{-1} , which mainly encompasses the bonding signatures between silicon, boron, and oxygen. Distinct peaks are present indicating absorption domains. The band regions are assigned based upon previous IR studies of borosilicate glass [116-118]. The band located at 680 cm^{-1} is associated with B-O-B bridging bonds, 800 cm^{-1} with Si-O-Si bending modes of bridging bonds, 920 cm^{-1} for B-O stretching within $\{\text{BO}_4\}$ tetrahedral borate units, 1025 cm^{-1} for asymmetric stretching of Si-O-Si bridges of connected silicate tetrahedra, 1150 cm^{-1} Si-O-B bonds, and 1350 cm^{-1} B-O stretching within $\{\text{BO}_3\}$ trigonal borate units. The spectra confirm structural differences from network former substitution specifically related to the conformation of the borate group. The prominent difference is in the proportion of borate that is configured in the charge compensated four-fold arrangement versus the trigonal borate. BS15.7 has the lowest relative ratio of absorbance peak intensities of four- to three-fold borate, and B7.5 has the highest ratio. The secondary spectral feature notable is the shift of the most intense normalized peak situated around 1000 cm^{-1} . That absorption band has been attributed to asymmetric vibrations of the Si-O-Si bridging between the silicate tetrahedra. As the fully

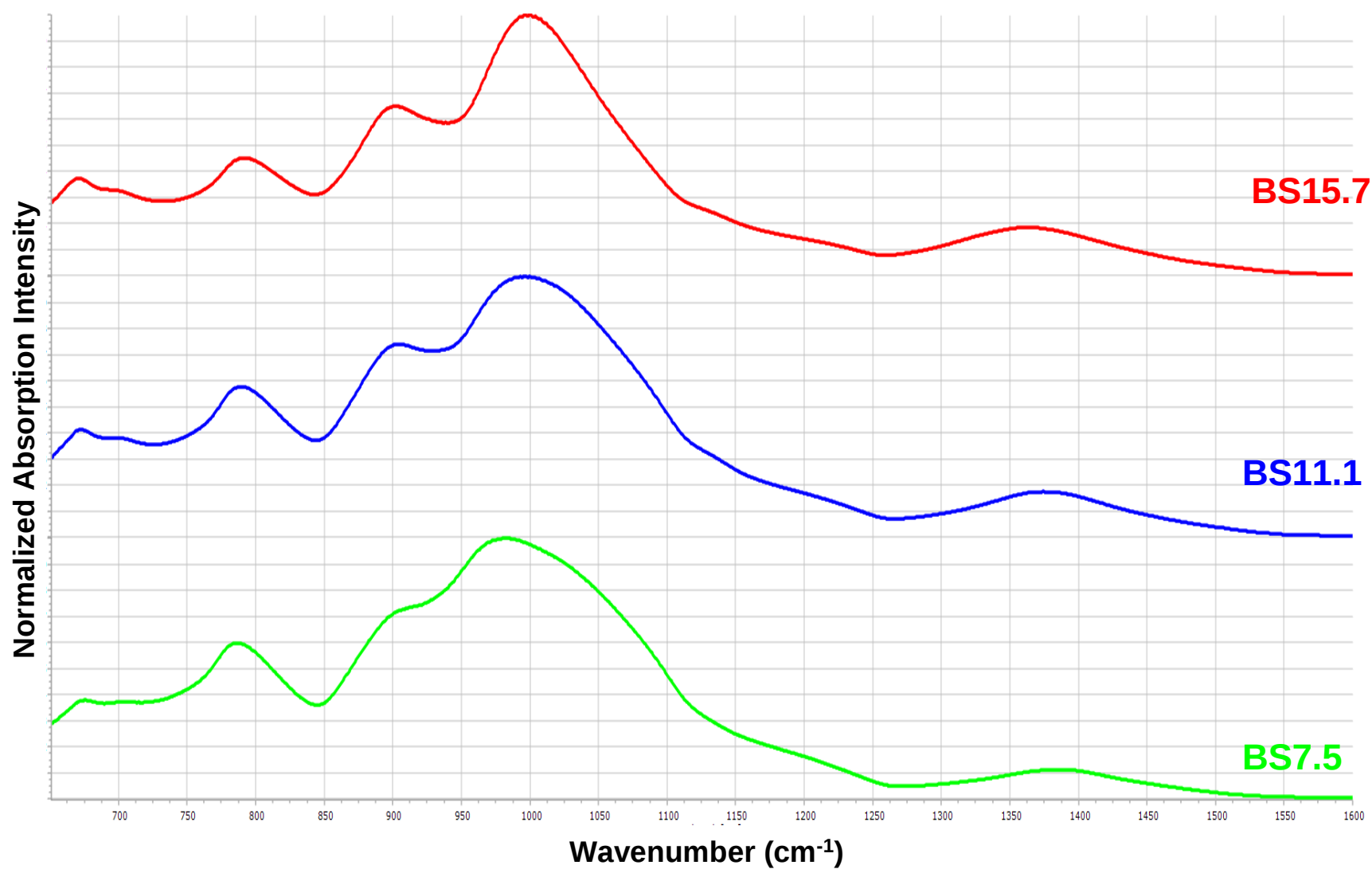


Figure 5.3: FTIR spectra of the three borosilicate compositions

polymerized network is disrupted by adding alkali network modifiers, for example, fewer silicate tetrahedra bridge to neighboring tetrahedra. The increase in non-bridging terminal oxygens could affect the infrared absorbance spectra through a visible shift of the Si-O- stretching band to lower wavenumbers (vibrational frequencies). However, a more likely alternative structural explanation for the apparent shift is convolution of two infrared absorption ranges. The greater proportion of four-fold coordinated borate would cause more overlap and mixing between the adjacent vibrational modes. The band assigned to B-O stretching within tetrahedral borate groupings becomes more of a shoulder of the Si-O stretching peak as tetrahedral borate concentration increases.

The eminently apparent structural trend for the three glasses is that substituting more silica for borate, increasing the silica to borate ratio while keeping the amounts of the other components constant, results in changes to the infrared absorption spectra that are consistent with a greater proportion of boron in tetrahedral coordination. The following section discussing the Raman data further supports this conclusion.

Structural characterization from Raman spectroscopy

FTIR was complemented with Raman spectroscopy to provide further insight into the base structures of the three borosilicates and to inform any connection to the yield stress. Raman spectroscopy is not redundant in this circumstance. Fig. 5.4 displays the Raman spectra for the three compositions. The addition of Raman spectroscopy activates a vibration mode must cause polarizability changes in a molecule. This means that some vibrations that were infrared active may not be Raman active and vice versa, uncovering more information in the process. Additional structural information regarding ring size and membership is provided by Raman spectroscopy of borosilicate glass. Micro-Raman spectroscopy of the glass samples was performed using excitation from a 514.5 nm argon-ion laser with a Raman shift from 250

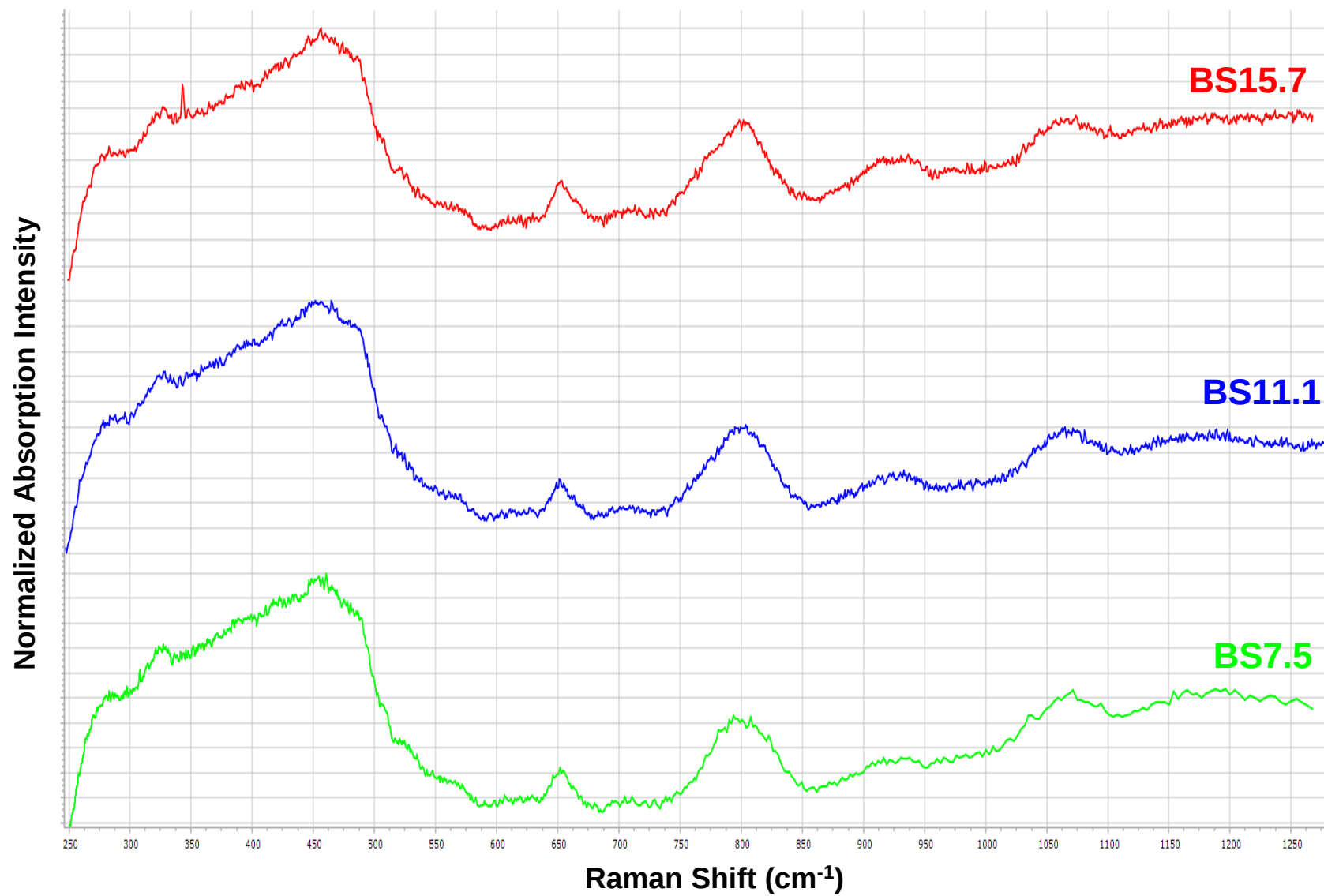


Figure 5.4: Raman spectra of the three borosilicate glass compositions

cm⁻¹ to 1275 cm⁻¹. Confocal optics focused the laser to a spot size of about 5 μm. From low to high wavenumbers, the spectral features are assigned to particular molecular vibration modes [118-122]. The broad swath of indicated intensity from 250 cm⁻¹ to 500 cm⁻¹ has been assigned to mixed stretching and bending modes of Si-O-Si and Si-O-B. The next prominent feature to the right is a peak at 650 cm⁻¹. This has often been ascribed to the breathing modes of isolated four-membered danburite-like ring structures, which consist of a {BO₄} unit bonding with another {BO₄} and three {SiO₄} tetrahedra, and conversely a {SiO₄} tetrahedra bonding with another {SiO₄} tetrahedra and three {BO₄} tetrahedra. In the 750-850 cm⁻¹ range there is a broad peak that may be deconvoluted into modes around 770 cm⁻¹ and 805 cm⁻¹, which correspond to {BO₄} and {BO₃} units respectively as a part of diborate and boroxol rings. The BS15.7 spectra are shifted closer to the 805 cm⁻¹ three-fold coordinated mode, and BS7.5 spectra are shifted more in the direction of the 770 cm⁻¹ four-fold coordinated mode. The next two bands (925 cm⁻¹ and 1060 cm⁻¹) are often associated with Si-O stretching of {SiO₄} tetrahedra with 2 and 1 non-bridging oxygen respectively, but the 925 cm⁻¹ band also could also represent other {BO₄} vibrational signatures [117]. Si-O stretching bands of {SiO₄} tetrahedra are weakly Raman active; the FTIR spectra, on the other hand, demonstrates strong activation and absorption intensity. The Raman data tell a similar story as did the FTIR. Apart from the self-evident differences in the relative number silicate to borate units between the three glasses, the three-fold versus four-fold borate coordination is the other prevailing structural difference resulting from varying the silicate to borate ratio and keeping the concentration of the other constituents constant.

Conclusions

Increases in the relative molar ratio of SiO₂ to B₂O₃ (K) correlate with increases in the yield stress. E and H also rose. Spectroscopy revealed that increasing the SiO₂ to B₂O₃ ratio increased the fraction of present tetrahedrally coordinated boron. The reason for the rise in all

three values describing resistances to deformation as K increased likely lies in the simple fact of there being more of the strongly bonded silicate tetrahedral groups compared to the number of planar borate triangles linked with comparably weaker binding forces. The larger fraction of tetrahedrally coordinated borate groups might also explain the stronger (σ_y), stiffer (E), and harder (H) trend as the molar ratio of SiO_2 to B_2O_3 increases owing to the greater network connectivity borne by tetrahedral rather than trigonal configuration.

Yield Stress and Densification from High Pressure DTDAC

A Double-Toroid Diamond Anvil Cell (DTDAC) was used to apply a (quasi)-hydrostatic pressure to machined baby aspirin-shaped 2.5 mm diameter glass samples shown in Fig. 5.5. Shear stresses are likely highest along the machined edges as well as due to the less-constrained periphery of the bulging middle section, all moving away from a pure hydrostatic stress described environment. The toroidal anvil was adapted into a modified Paris-Edinburgh press pictured in Fig. 5.6. The anvil itself was made centrally of polycrystalline diamond surrounded by a cylinder composed of tungsten carbide. Steel rings were used for the gasket assembly, and the oil pressure was set corresponding to calibrated sample incremental pressure values stepping from 2 GPa to 14 GPa. While this does not provide a direct measure of the internal sample pressure, a rough indication of pressure still adequately performs the task of supplying incremental potential pressure-induced changes within the sample.

Density changes

The degree of densification was tracked by comparing the density of the glass samples after being pressurized to the initial standard temperature and atmospheric pressure condition. The state of the samples after their trial in the pressure cell varied. Oftentimes, the two ends of the aspirin-shaped samples would shear off intact along with small fragments of the former middle section. This indicates that the state of stress present is not purely hydrostatically

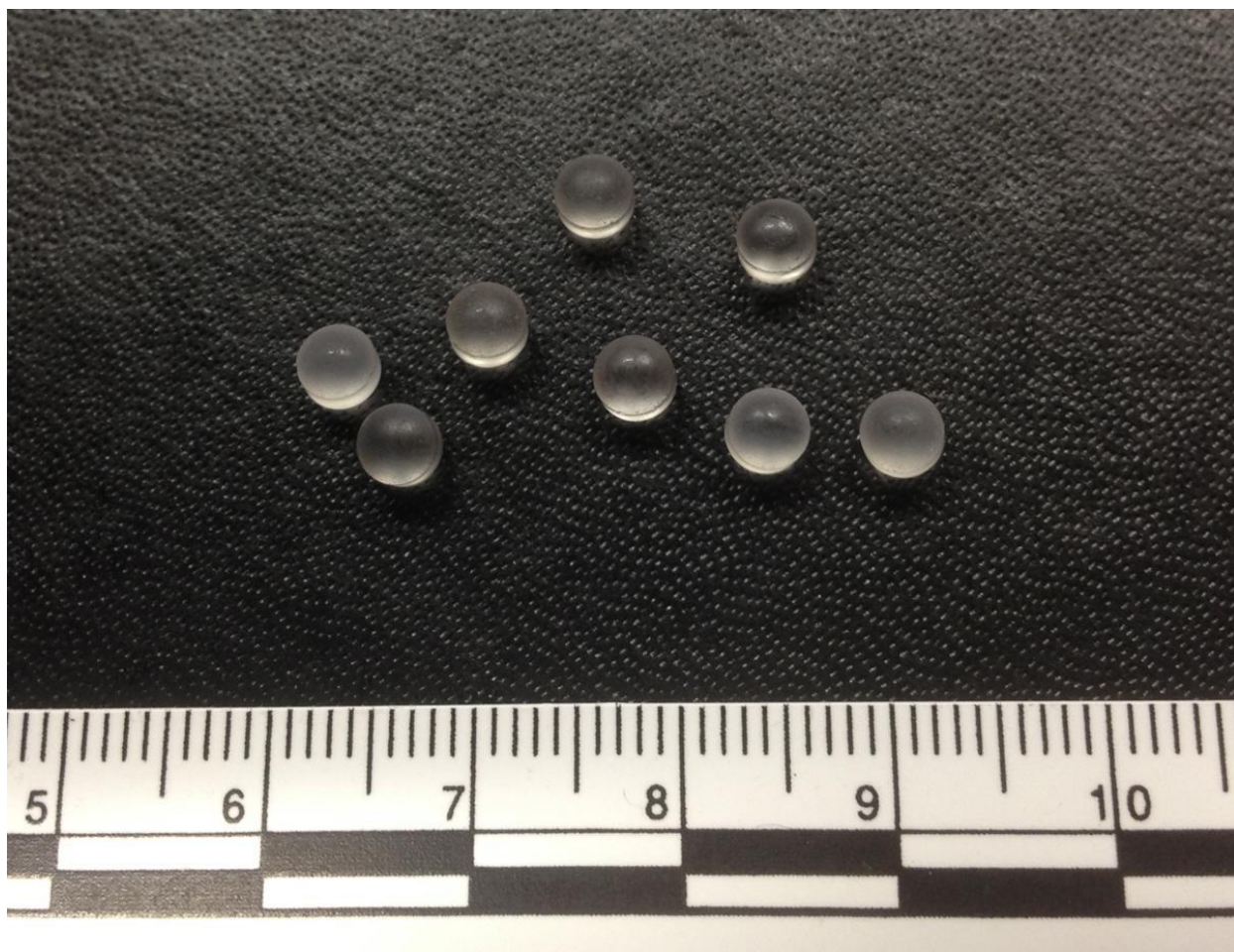


Figure 5.5: Size and shape of glass specimens machined for DTDAC testing



Figure 5.6: Paris-Edinburgh press apparatus

compressive in nature. Despite the samples being reduced to many pieces, density was obtained through direct means. Small volumes of the sample remnants were floated in a dense lithium metatungstate liquid whose density could be precisely controlled. The density was recorded according to the following standard: the density of the fluid was increased until a final fragment was stably suspended. This density is representative of the maximum degree of densification achieved within the sample as a whole. It is not an average density of the entire sample. The variation of fragment densities again lends support to the notion of shear-enhanced densification susceptibility since the localized states of stress within the sample are not constant. Regrettably, without knowing the actual statistical variation of the fragment densities or the precise localized stress variations, a definitive relationship between the two remains not fully substantiated.

Even though the reported density is systematically biased in favor of the fragment with the highest density, this did not detract from the use of density as an indicator of structural rearrangement and character. Substituting Si units with B units depressed the density. Permanent densification is shown as a function of maximum pressure in Fig. 5.7. All of the glasses exhibit a densification threshold between 6 and 10 GPa. Because of the likely deviations from pure hydrostatic pressure conditions along with the density measurement technique which is skewed toward the fragments with the highest density, the threshold pressure for densification is likely lower than for a purely hydrostatic loading, just as Sakka and Mackenzie [29] showed in Fig. 2.3.

Effect of DTDAC testing on yield stress and other mechanical parameters

Fragments of the glass samples formed after DTDAC testing were collected and following float density measurement were mounted in an epoxy resin, which was polished according to the same water-free procedures outlined in Chapter IV. Distinct changes in indentation deformation characteristics are observed when comparing the glasses before and

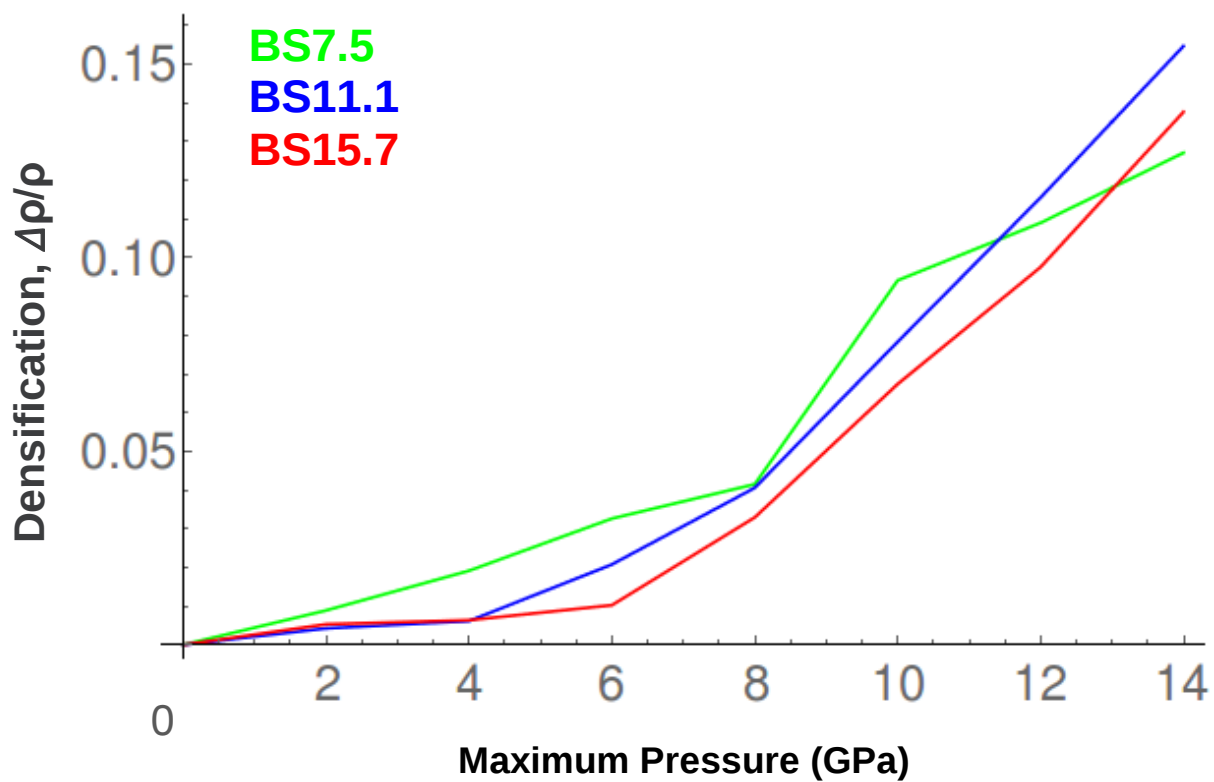


Figure 5.7: The permanent densification amounts measured by float density of fragments of each glass composition after subjection to high-pressure in a DTDAC

after being subjected to DTDAC compression up to 12 GPa. Shifts of the load-displacement curves leftward following DTDAC treatment, as seen in Fig. 5.8 comparing the most disparate glass compositions and pressure conditions, signal that each glass became more resistant to deformation. Increases in indentation hardness and elastic modulus echoed this too. Elastic modulus and indentation hardness of BS7.5 and BS15.7 are plotted as function of indenter depth of penetration in Fig. 5.9 and Fig 5.10. The yield stress also increased after high pressure confinement to 12 GPa. S^3/P divergent curves used to determine the yield stress of the 0 and 12 GPa maximum applied pressure of the triad of glasses are shown in Fig. 5.11, Fig. 5.12, and Fig. 5.13 for BS7.5, BS11.1, and BS15.7 respectively. These changes are correlated to the density changes resulting from densification processes. The relative magnitude of the jumps in deformation properties after densification caused by high pressure was not consistent across the three glasses. So while the indentation hardness, elastic modulus, and yield stress was the highest for BS7.5 after 12 GPa DTDAC pressurization, the greatest relative change from the unpressurized state to 12 GPa happened for BS15.7. The prospect for mechanical property enhancement via densification thus may be heightened for BS15.7. The reason for the difference may be differences in the influence of shearing component of deformation along with the greater diversity of avenues for densification borate structures avail themselves to because of their higher free volume. Expanding on the latter reason, the upper limit of permanent densification amount for fused silica is observed to be higher than borate glass while borate glasses have much lower thresholds for densification [28]. The effect of pressure on the mechanical properties derived from indentation is tabulated in Table 5.2. The increases in indentation hardness, elastic modulus, and yield stress all correlate with increases in density. For BS7.5, a sequence pressures shows that the density and deformation properties are closely linked. A distinct threshold is present below which little change in either density or measured mechanical properties is observed (0 - 4 GPa), and above which abrupt increases in indentation hardness, elastic modulus, and yield stress occur (8 -12 GPa). Due to the aforementioned

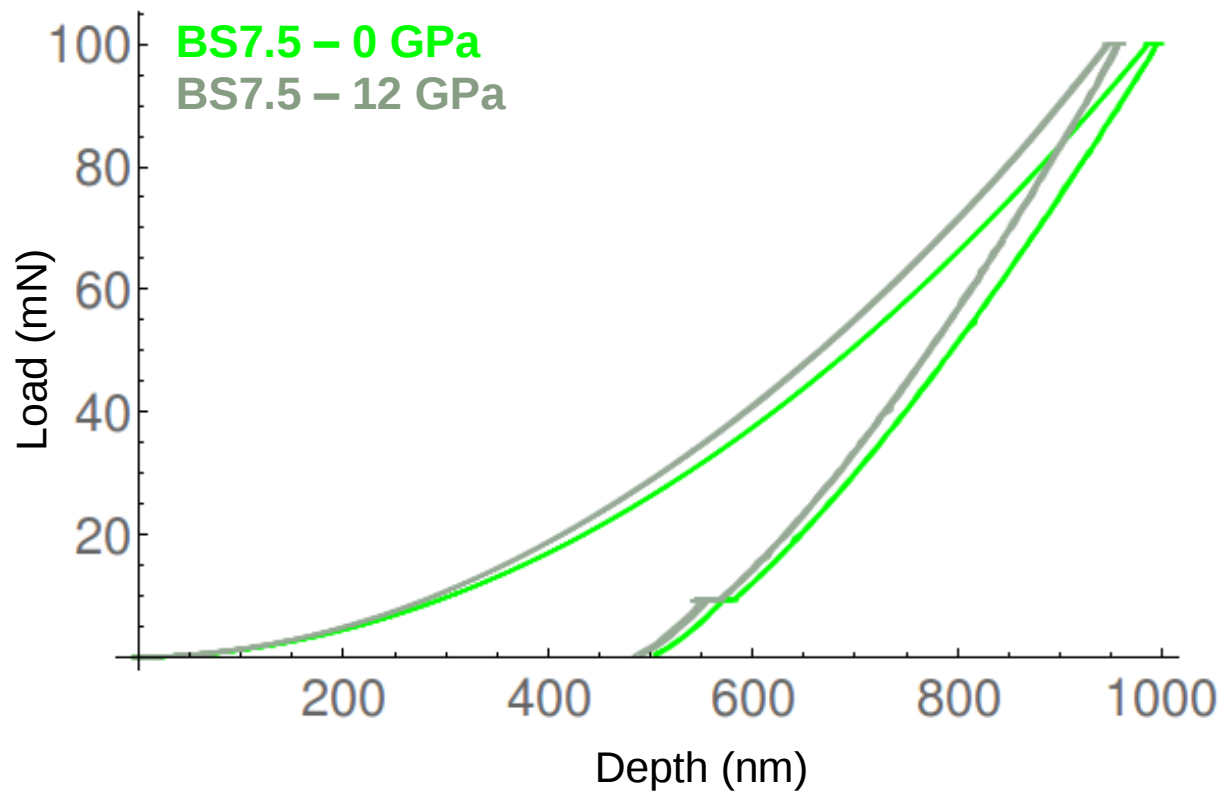
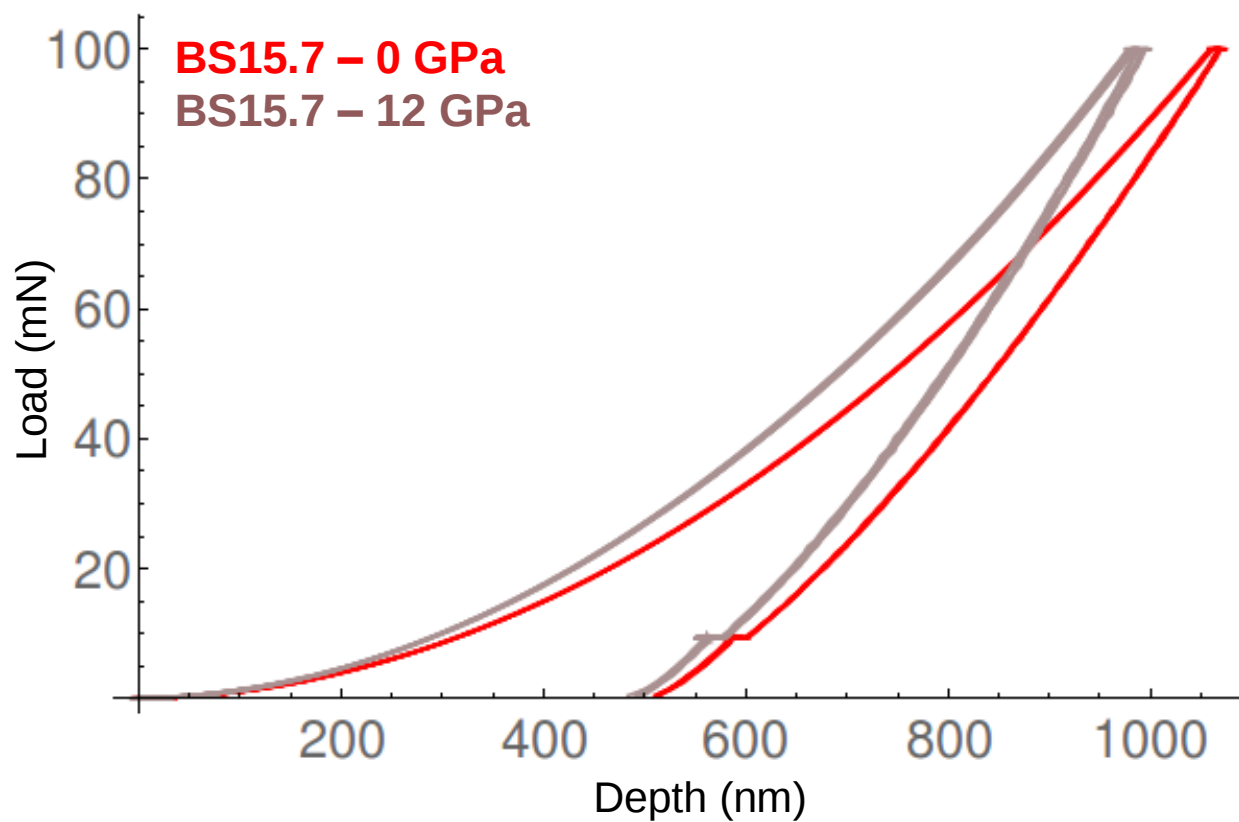


Figure 5.8: The difference in load as a function of indenter depth from the baseline 0 GPa and 12 GPa is shown for BS15.7 (Top) and BS7.5 (Bottom).

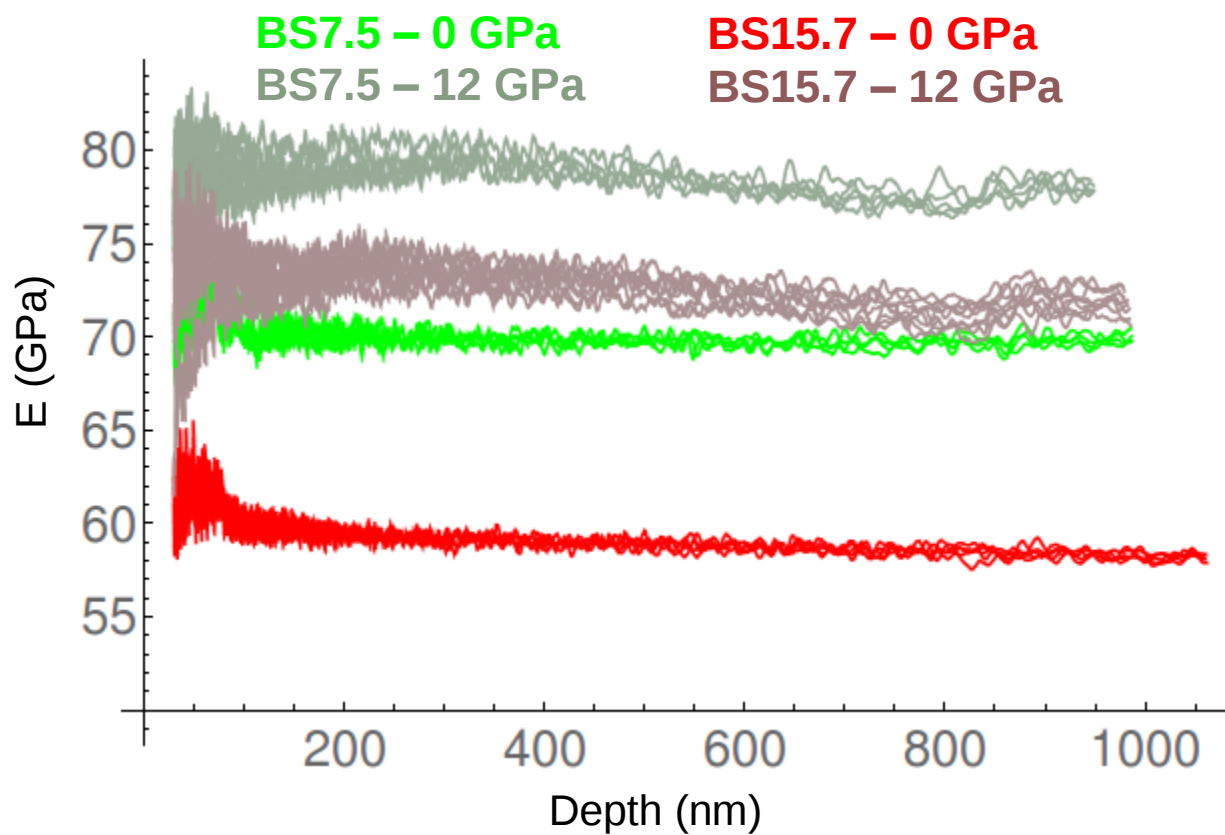


Figure 5.9: Elastic modulus as a function of indentation depth from Berkovich nanoindentation comparing the extremes of both compositional and maximum pressure difference.

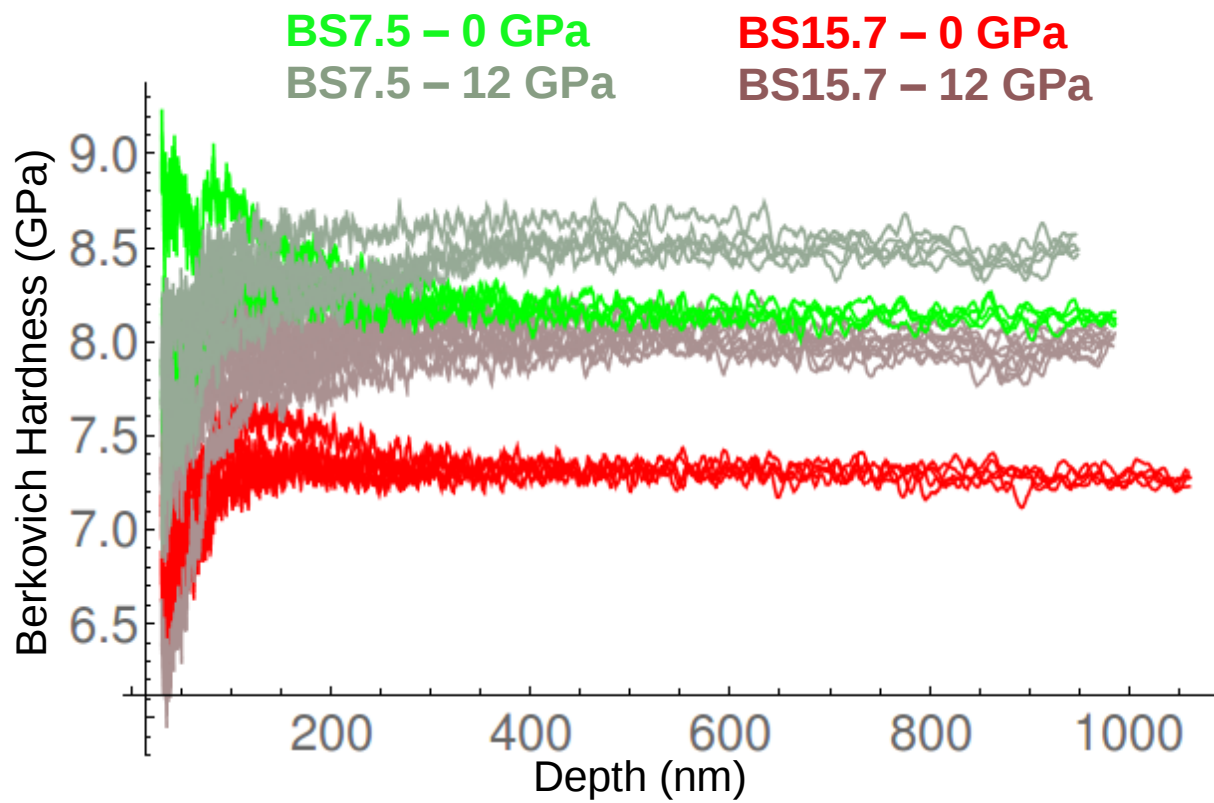


Figure 5.10: Indentation hardness as a function of indentation depth from Berkovich nanoindentation comparing the extremes of both compositional and maximum pressure difference.

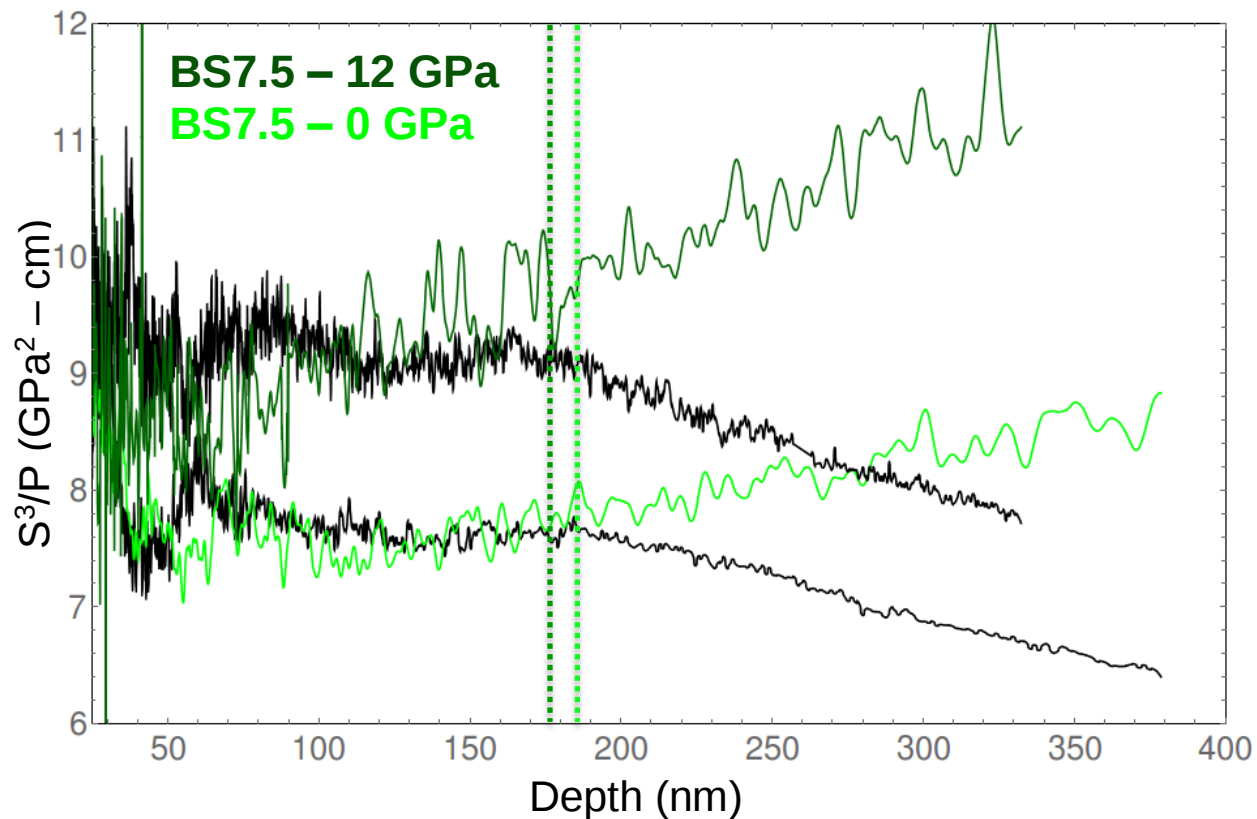


Figure 5.11: S^3/P as a function of $3.2\ \mu\text{m}$ spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS7.5 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).

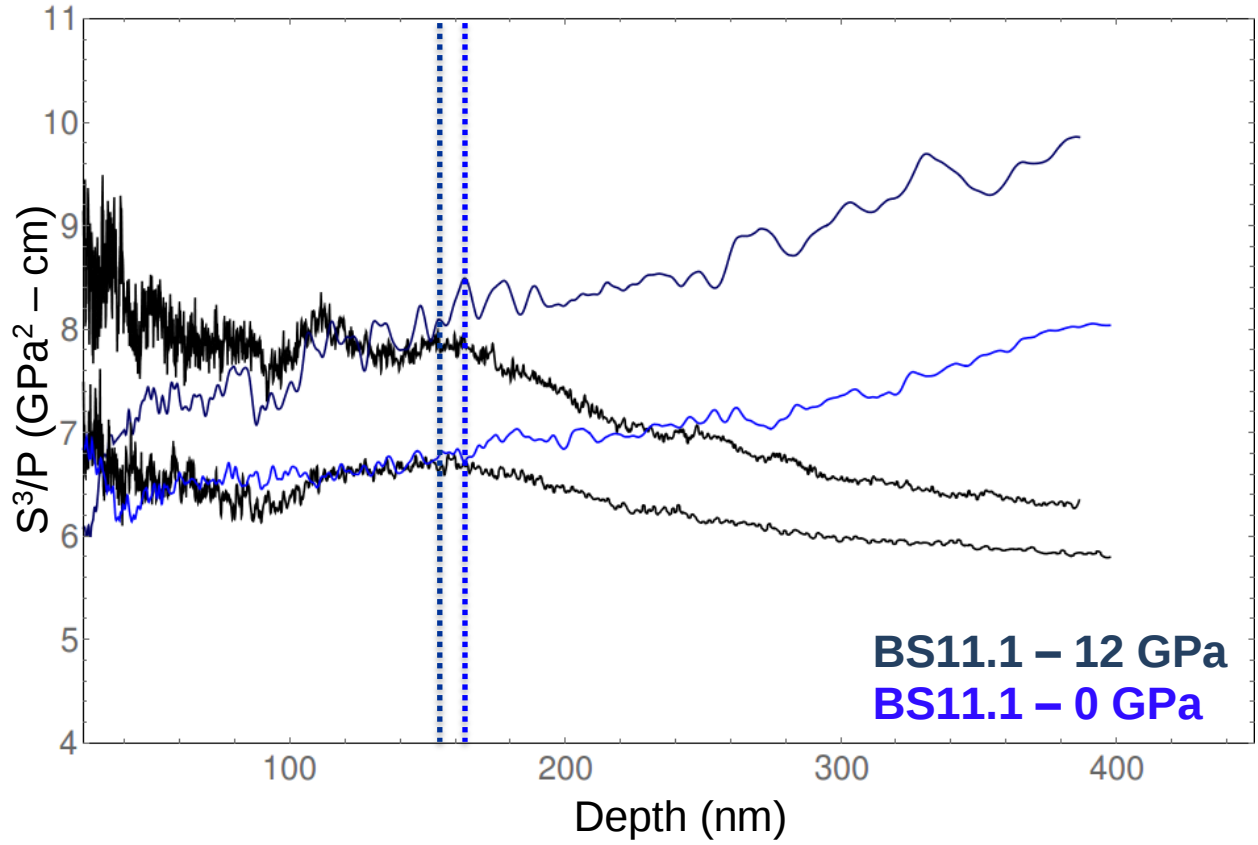


Figure 5.12: S^3/P as a function of $3.2\ \mu\text{m}$ spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS11.1 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).

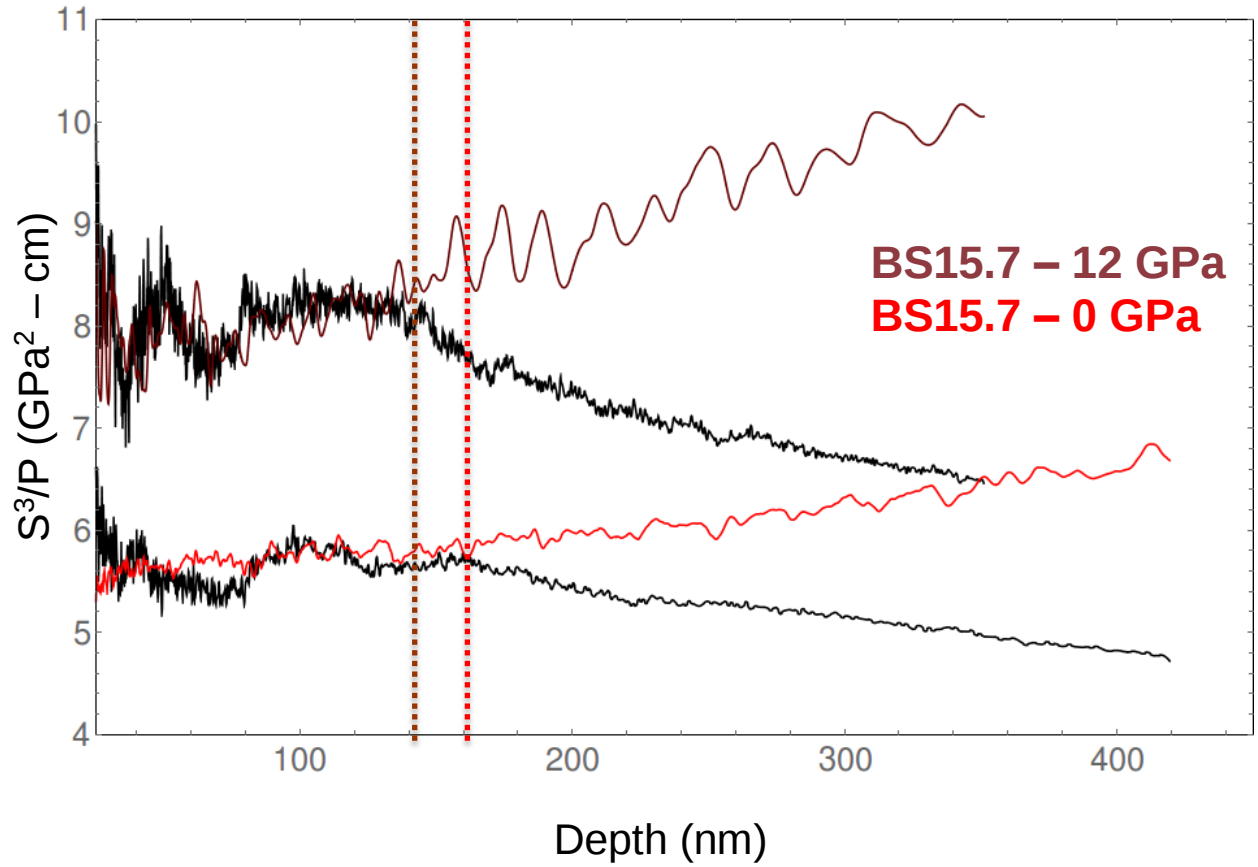


Figure 5.13: S^3/P as a function of $3.2\ \mu\text{m}$ spherical indentation depth comparing the 0 GPa and 12 GPa conditions of BS15.7 post pressurization. The dotted vertical lines mark the divergence point of the two stiffness sources for each glass (colored for continuous dynamic stiffness measurement and black for interpolated loading stiffness).

highest density bias of the density measurements, it is to be expected that the measured bulk mechanical properties and parameters lag with changes being seen at higher pressures in comparison to the changes observed in the density. The relative changes in yield stress most closely correspond to the relative density changes and without any lag for BS7.5. The coincident changes of yield stress and density mean that the yield surface is expanding outwards due to a kind of hardening induced by densification. The near one to one proportionality of the changes of density and yield stress due to pressure is intriguing as it could suggest that yield stress is closely associated with densification and also that yield stress measurement captures information central to the mechanics of the densification process, especially with regard to how the yield surface is altered. One mechanical parameter that was observed to decrease as the glass densified was the constraint factor. A drop of the constraint factor could indicate hardening with an increase in overall elastic character versus plastic shearing deformation.

The S^3/P curves for the 12 GPa samples do not track each other as well as the baseline 0 GPa samples. This could be the result of the epoxy mount lowering the frame stiffness of the contact system. A question that might be raised when analyzing the S^3/P curves is whether densification would be detectable in some way. Since the indentation process involves invocation of shear and hydrostatic stresses underneath the region of contact, this has the potential of causing the same densifying deformation process that occurs with the anvil cell pressurization. The analytical expression for S^3/P does indeed include a squared reduced elastic modulus term. Therefore, if indeed the modulus has appreciably changed, as is the case with the high pressure anvil cell experiments, then why wouldn't the S^3/P curve also be sensitive to this change? The answer may be that the volume of material subjected to density changes is small compared to the stiffness contribution of all of the surrounding material, the elastic hinterland, whose elastic properties remain unchanged. Other parasitic factors such as cracking and pile-up, too, begin to creep in as the indent enlarges.

Structural characterization of densified glass using Raman spectroscopy

As with the effect of composition on the structure and mechanical properties, the connection between the observed mechanical property changes associated with high pressure induced densification and the structure was probed using Raman spectroscopy. Telltale signs of spectral differences linked to densification processes are seen in Fig. 5.14. Across all three glass compositions, similar features are present when comparing the baseline 0 GPa glass to the glass samples subjected to 12 GPa pressure. Pointing out the differences moving from low wavenumbers to high, first there is a subtle shift to higher wavenumbers and increase in absorption intensity of the most prominent high frequency segment of the broad band of 300 cm^{-1} to 500 cm^{-1} . This kind of upward shift of bending modes of Si-O-Si bonds has been linked to decreases in bonding angles and a shift to smaller silicate ring sizes, packing in the silicate network more tightly [32]. The next difference is a downward shift in the band centered around 650 cm^{-1} usually assigned to ring structures containing interlinked borate and silicate in danburite-like configurations. Such a shift would signal a rearrangement of those mixed structures. The theme of rearrangement of networked structures is particularly marked for the band originally spanning from 750 cm^{-1} to 850 cm^{-1} . In each case, the lower frequency side of the band is diminished for the densified 12 GPa glasses. That 770 cm^{-1} band is attributed to three-membered borate rings containing a tetrahedral borate unit. The 805 cm^{-1} band remains steady and is associated with boroxol rings. From this observation, it can be concluded that densification in these glasses results in the preferential breakdown of those three-membered tetrahedral borate containing ring structures as opposed to the boroxol rings. This tendency has been described by [122] for other low alkali borosilicate glasses. The band centered about 925 cm^{-1} is linked to this same phenomena. This band represents the stretching modes of tetrahedral borate units. Its diminishment again underscores the major structural change seen with the borate subnetwork upon pressurization: the breakup of four-coordinated borate containing rings. The final difference that appears in the Raman spectra following DTDAC

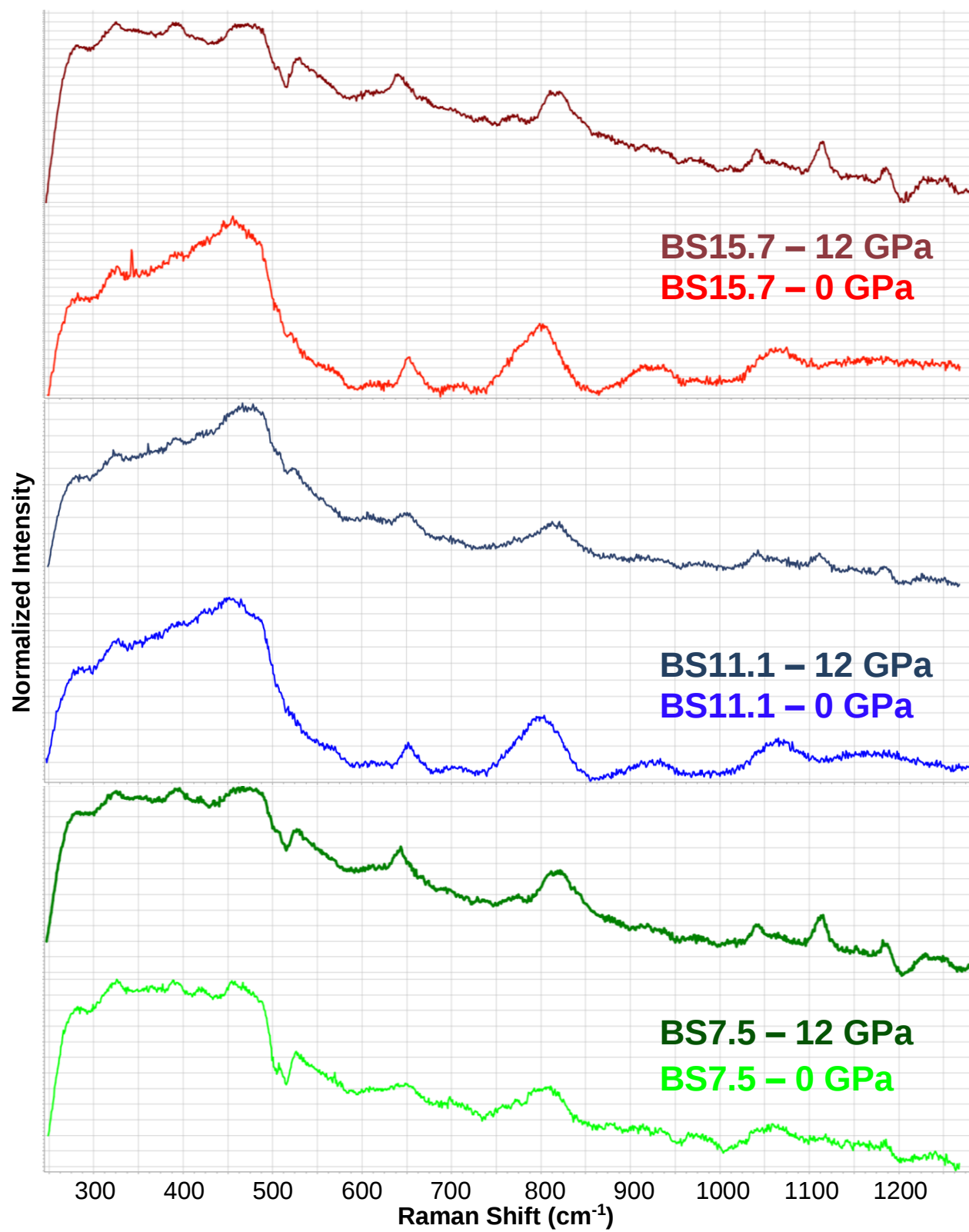


Figure 5.14: Raman spectra of 0 GPa and 12 GPa pairs of each borosilicate glass composition

pressurization and subsequent permanent deformation are three well-defined peaks (1045, 1110, and 1185 cm^{-1}). No matching occurrences of this series of distinct peaks have been reported in the literature. Bands in this range for borosilicate glasses are normally assigned to the stretching of Si-O- housed in tetrahedra, but being weakly Raman active, there is no expectation for distinct peaks to suddenly form in this region of the spectra because of densifying processes. Given that even the 4 GPa BS7.5 sample, which did not show any density or mechanical property changes and thus is likely below the threshold for densification, contained the trio of peaks, the source may not be associated with structural densification changes at all.

Conclusions

The Raman spectra revealed some active mechanisms responsible for permanent compaction and accompanying increases in indentation hardness, elastic modulus, and yield stress. The compacted structure became more resistant to deformation overall. Each composition responded similarly from the standpoint of changes in structure and mechanical properties. The main difference between how the compositions responded to the high DTDAC pressure was that BS15.7 exhibited relatively greater changes in density and mechanical properties likely as a consequence of it having the most free volume to start with and hence a greater capacity for densification.

Process of Discovery of Yield Surface Boundary

The structural changes that may occur under nominally hydrostatic loading conditions informs as to what contribution densification has to observed mechanical properties. The interrelated pair between mechanical properties and structure is examined as a function of imposed hydrostatic pressure conditions. The other supplemental contextual element is an extension of the mechanical and structural analysis to glass samples which were subjected to

varied amounts of confining hydrostatic pressure in a pressure cell. Information gleaned from the case of purely hydrostatic compression enables the mixed pressure conditions (shear accompanied with hydrostatic component) of yielding under an applied spherical indentation contact load to be more wholly understood.

A series of parabolic-like curves in Fig. 5.15 shows the state of stress along the central axis of a spherically indented surface, growing as the applied force increases. The end of the curve corresponds to the stress state at the surface and the origin of the curve is the stress state infinitely down the central z-axis where the stress is zero. A snapshot of the state of stress at yielding is displayed in Fig. 5.16. In the testing carried out in this work, two points on the curve can be given. They are found from 1.) the mixed (hydrostatic-shear) stress field from spherical indentation and 2.) the nominally hydrostatic stress field from anvil cell compression. A portrayal of the two points is provided in Fig. 5.17. Also shown are two common yield criteria: the constant maximum strain energy stress criteria (von Mises), and the Drucker-Prager type elliptical pressure dependent yield surface when viewed in the shear stress versus hydrostatic stress plane. If additional yield stress critical points could be plotted from other triaxial loading conditions, the real yield surface could be formed.

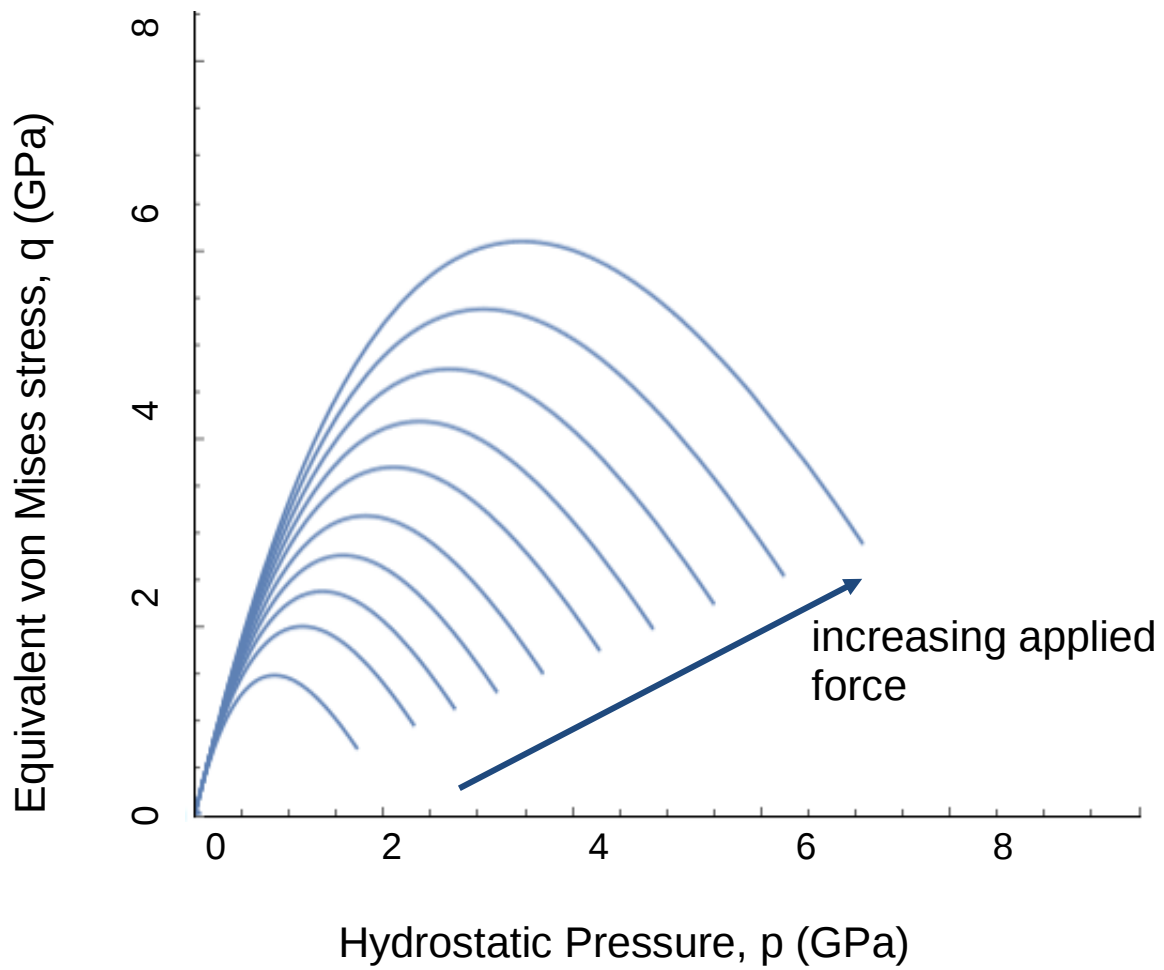


Figure 5.15: The progressive state of stress along the central axis of a material indented with a sphere as the applied force increases.

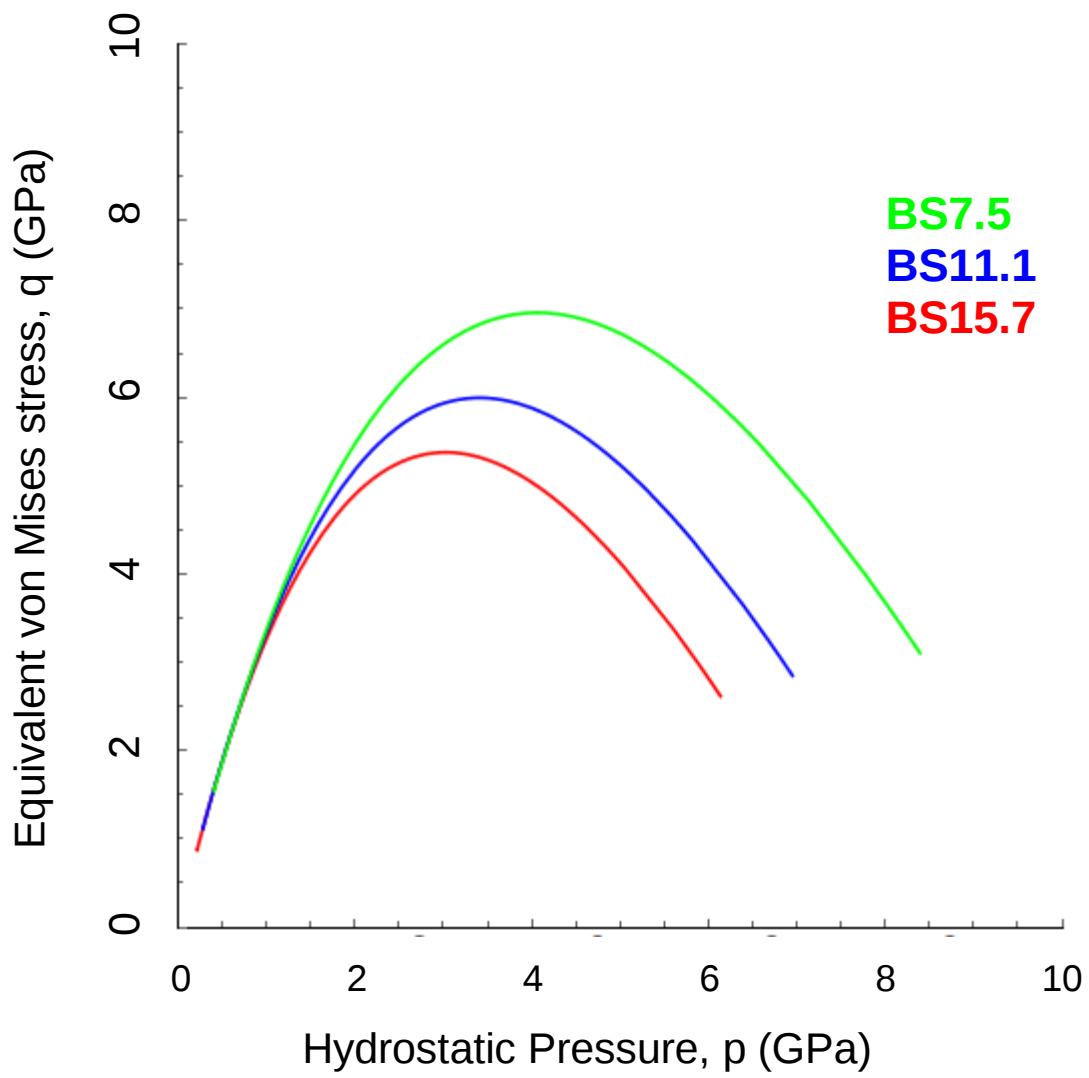


Figure 5.16: A snapshot of the state of stress along the central axis at the point of yielding.

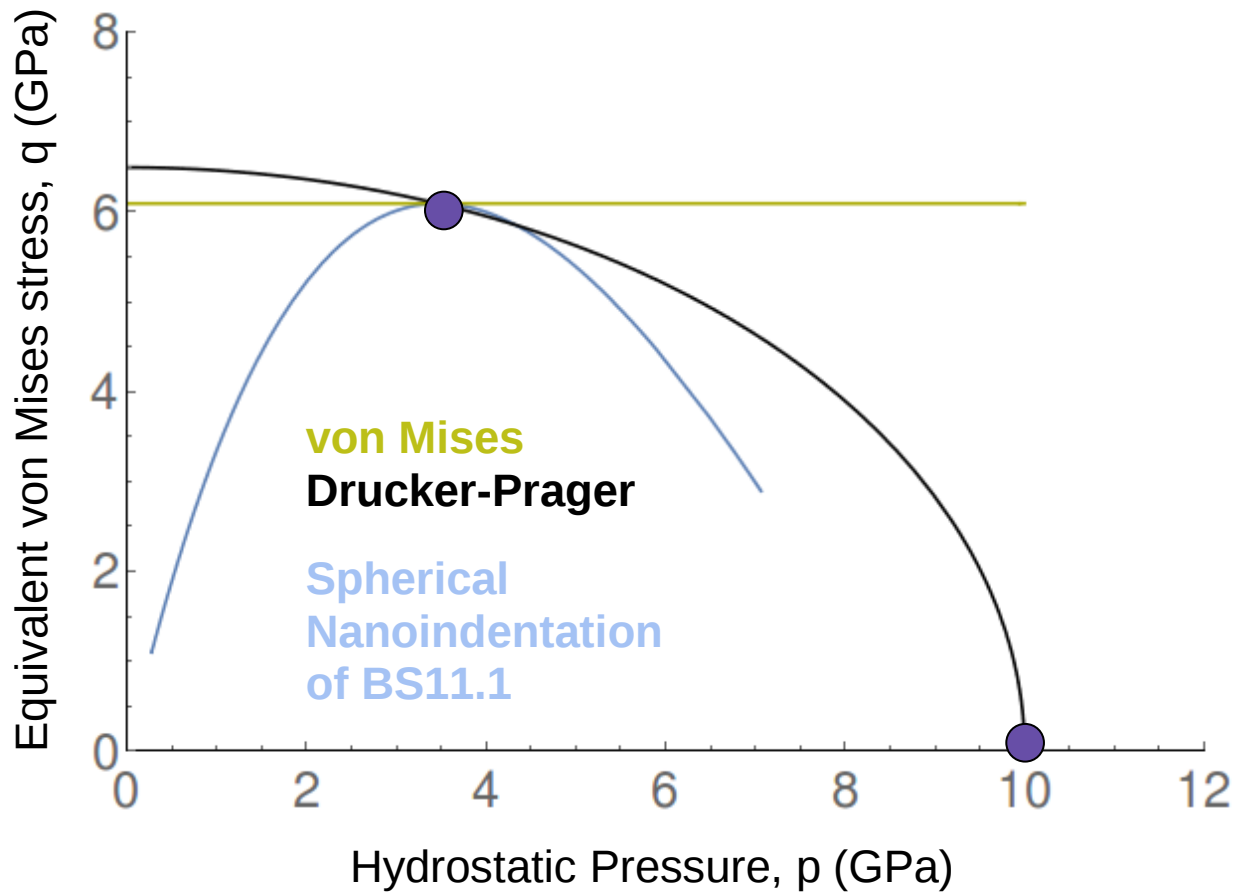


Figure 5.17: Two purple points mark the yield point determined through spherical indentation of BS11.1 and the point on the x-axis corresponds to the threshold pressure for densification of an ideally pure hydrostatic loading condition. The state of stress during spherical indentation is shown in blue along with two common yield criteria that could be fit as tangent to the indentation stress state.

CHAPTER VI: CONCLUSIONS

The transition from purely elastic deformation to non-elastic deformation has acute implications for design and mechanical modeling principles including ballistic impact. The primary motive of this work was to determine the yield stress of three low-alkali borosilicate glasses whose composition varied according to substitutions between SiO_2 and B_2O_3 . To achieve this, a new method was developed featuring a derived elastically invariant parameter of S^3/P from spherical indentation, which exploits the gradual progression of contact pressure that spherical geometry imposes. The S^3/P parameter relays changes in the effective radius of curvature of the contact caused by yielding and the accompanying formation of a permanent impression. The method, first applied in a comparison of two archetypal normal and anomalous glasses (soda-lime silicate and fused silica), found a 2 GPa difference in yield stress. Yield stress measurements for all inorganic glasses tested were consistent across two different tip radii sizes.

Corroboration of yield stress values obtained from the new method and uniaxial compression tests of the same material, titanium, were successful. The same cannot be said of bulk metallic glass or tungsten in this experimental set-up because of a localization of deformation at the diminutive scales involved in nanoindentation invalidating bulk continuum descriptions of deformation necessary for yield stress agreement between the two methods.

The process of preparing the borosilicate sample surfaces for the application of the new indentation technique uncovered a disruptive effect water has on the accurate measurement of bulk material properties using indentation. The borosilicate glass containing the most borate had the highest susceptibility to water incursion and the largest drop of elastic modulus and hardness at the surface. The source of the reduced surface mechanical properties is an altered water-containing porous surface layer. Water-free surface planarization procedures should be undertaken to avoid this issue.

The trend observed for the three borosilicate glasses was that the yield stress increased as the SiO_2 to B_2O_3 ratio (K) increased. Changes in elastic modulus and indentation hardness

followed the same increasing trend. Structural information consisted of vibrational spectra and density measurements. The structural features linked to increases in yield stress as K increases are increases in tetrahedrally arranged silicate groups at the expense of the trigonal planar borate subnetwork and corresponding increases in the fraction of boron in tetrahedral configuration. The increase in more strongly bonded silicate groups and of the relative amount tetrahedrally coordinated groups overall gives rise to higher measured yield stress.

Subjecting the borosilicate glasses to high hydrostatic pressure in a DTDAC permanently densified all three glasses once past a threshold pressure. Increases in density corresponded with increases in yield stress, elastic modulus, and indentation hardness. The structural changes caused by densification and associated with rises in yield stress mainly involved the compaction of the silicate subnetwork through bond angle shortening and the breakdown of ring structures containing tetrahedrally coordinated borate.

The herein developed yield stress determination technique has the potential to be applied to map out a yield surface when used in combination with other high pressure confinement techniques, further advancing understanding of high-pressure-induced structural changes in vitreous borosilicates and the relationship between hydrostatic and shear stresses on the resulting deformation processes.

LIST OF REFERENCES

- [1] Chocron, Sidney, et al. "Constitutive model for damaged borosilicate glass under confinement." *Journal of the American Ceramic Society* 90.8 (2007): 2549-2555.
- [2] Grujicic, M., et al. "A ballistic material model for starphire®, a soda-lime transparent-armor glass." *Materials Science and Engineering: A* 491.1 (2008): 397-411.
- [3] Grujicic, Mica, W. C. Bell, and Bhaskar Pandurangan. "Design and material selection guidelines and strategies for transparent armor systems." *Materials & Design* 34 (2012): 808-819.
- [4] Forde, L. C., et al. "Ballistic impact studies of a borosilicate glass." *International Journal of Impact Engineering* 37.5 (2010): 568-578.
- [5] Debenedetti, Pablo G., and Frank H. Stillinger. "Supercooled liquids and the glass transition." *Nature* 410.6825 (2001): 259-267.
- [6] Fischer, Henry E., Adrian C. Barnes, and Philip S. Salmon. "Neutron and x-ray diffraction studies of liquids and glasses." *Reports on Progress in Physics* 69.1 (2005): 233.
- [7] Greaves, G. N., and S. Sen. "Inorganic glasses, glass-forming liquids and amorphizing solids." *Advances in Physics* 56.1 (2007): 1-166.
- [8] Zachariasen, William Houlder. "The atomic arrangement in glass." *Journal of the American Chemical Society* 54.10 (1932): 3841-3851.
- [9] Wright, A. C., and M. F. Thorpe. "Eighty years of random networks." *physica status solidi (b)* 250.5 (2013): 931-936.
- [10] Du, L-S., et al. "Pressure-induced structural changes in a borosilicate glass-forming liquid: boron coordination, non-bridging oxygens, and network ordering." *Journal of Non-Crystalline Solids* 337.2 (2004): 196-200.
- [11] Smedskjaer, Morten M., et al. "Topological principles of borosilicate glass chemistry." *The Journal of Physical Chemistry B* 115.44 (2011): 12930-12946.
- [12] Meera, B. N., and J. Ramakrishna. "Raman spectral studies of borate glasses." *Journal of Non-Crystalline Solids* 159.1-2 (1993): 1-21.
- [13] Ferlat, Guillaume, et al. "Boroxol rings in liquid and vitreous B₂O₃ from first principles." *Physical review letters* 101.6 (2008): 065504.
- [14] Jellison, G. E., and P. J. Bray. "A structural interpretation of B10 and B11 NMR spectra in sodium borate glasses." *Journal of Non-Crystalline Solids* 29.2 (1978): 187-206.
- [15] Chrysikos, Georgios D., E. I. Kamitsos, and M. A. Karakassides. "Structure of borate glasses. II: Alkali induced network modifications in terms of structure and properties." *Physics and chemistry of glasses* 31.3 (1990): 109-116.
- [16] Möncke, Doris, et al. "Thermal history of a low alkali borosilicate glass probed by infrared and Raman spectroscopy." *Glass Technology-European Journal of Glass Science and Technology Part A* 47.5 (2006): 133-137.
- [17] Cormier, L., et al. "Temperature-Induced Structural Modifications Between Alkali Borate Glasses and Melts." *Journal of the American Ceramic Society* 89.1 (2006): 13-19.
- [18] Wang, Shuanhu, and Jonathan F. Stebbins. "Multiple-Quantum Magic-Angle Spinning 17O NMR Studies of Borate, Borosilicate, and Boroaluminate Glasses." *Journal of the American Ceramic Society* 82.6 (1999): 1519-1528.
- [19] Bunker, B. C., et al. "Multinuclear nuclear magnetic resonance and Raman investigation of sodium borosilicate glass structures." *Physics and chemistry of glasses* 31.1 (1990): 30-41.
- [20] Baltisberger, J. H., et al. "Triple-quantum two-dimensional 27Al magic-angle spinning nuclear magnetic resonance spectroscopic study of aluminosilicate and aluminate crystals and glasses." *Journal of the American Chemical Society* 118.30 (1996): 7209-7214.
- [21] Zheng, Qiuju, et al. "Composition–structure–property relationships in boroaluminosilicate glasses." *Journal of Non-Crystalline Solids* 358.6-7 (2012): 993-1002.

- [22] Yun, Y. H., and P. J. Bray. "Nuclear magnetic resonance studies of the glasses in the system Na₂O B₂O₃ SiO₂." *Journal of Non-Crystalline Solids* 27.3 (1978): 363-380.
- [23] Dell, W. J., P. J. Bray, and S. Z. Xiao. "¹¹B NMR studies and structural modeling of Na₂O B₂O₃ SiO₂ glasses of high soda content." *Journal of Non-Crystalline Solids* 58.1 (1983): 1-16.
- [24] Egami, Takeshi. "Atomic level stresses." *Progress in Materials Science* 56.6 (2011): 637-653.
- [25] Rouxel, Tanguy, et al. "Poisson's ratio and the densification of glass under high pressure." *Physical review letters* 100.22 (2008): 225501.
- [26] El-Moneim, A. Abd. "Quantitative analysis of elastic moduli and structure of B₂O₃-SiO₂ and Na₂O-B₂O₃-SiO₂ glasses." *Physica B: Condensed Matter* 325 (2003): 319-332.
- [27] Mackenzie, J. D. "High-Pressure Effects on Oxide Glasses: I, Densification in Rigid State." *Journal of the American Ceramic Society* 46.10 (1963): 461-470.
- [28] Bridgman, P. W., and I. Šimon. "Effects of very high pressures on glass." *Journal of applied physics* 24.4 (1953): 405-413.
- [29] Sakka, S., and J. D. Mackenzie. "High pressure effects on glass." *Journal of Non-Crystalline Solids* 1.2 (1969): 107-142.
- [30] Benmore, C. J., et al. "Structural and topological changes in silica glass at pressure." *Physical Review B* 81.5 (2010): 054105.
- [31] Perriot, Antoine, et al. "Raman microspectroscopic characterization of amorphous silica plastic behavior." *Journal of the American Ceramic Society* 89.2 (2006): 596-601.
- [32] Hemley, R. J., et al. "Raman Spectroscopy of SiO₂ Glass at High Pressure." *Physical Review Letters* 57.6 (1986): 747.
- [33] Svenson, Mouritz N., et al. "Composition-structure-property relations of compressed borosilicate glasses." *Physical Review Applied* 2.2 (2014): 024006.
- [34] Brazhkin, V. V., et al. "Nature of the structural transformations in B₂O₃ glass under high pressure." *Physical review letters* 101.3 (2008): 035702.
- [35] Lee, Sung Keun, et al. "Probing of bonding changes in B₂O₃ glasses at high pressure with inelastic X-ray scattering." *Nature Materials* 4.11 (2005): 851-854.
- [36] Wondraczek, Lothar, et al. "Structure-energy map of alkali borosilicate glasses: Effects of pressure and temperature." *Physical Review B* 76.1 (2007): 014202.
- [37] Østergaard, Martin B., et al. "Temperature-dependent densification of sodium borosilicate glass." *RSC Advances* 5.96 (2015): 78845-78851.
- [38] Reibstein, Sindy, et al. "Structural heterogeneity and pressure-relaxation in compressed borosilicate glasses by in situ small angle X-ray scattering." *The Journal of chemical physics* 134.20 (2011): 204502.
- [39] Marsh, D. M. "Plastic flow in glass." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 279. No. 1378. The Royal Society, 1964.
- [40] Wakabayashi, Daisuke, Nobumasa Funamori, and Tomoko Sato. "Enhanced plasticity of silica glass at high pressure." *Physical Review B* 91.1 (2015): 014106.
- [41] Peter, K. W. "Densification and flow phenomena of glass in indentation experiments." *Journal of Non-Crystalline Solids* 5.2 (1970): 103-115.
- [42] Kermouche, G., et al. "Perfectly plastic flow in silica glass." *Acta Materialia* 114 (2016): 146-153.
- [43] Kermouche, Guillaume, et al. "Mechanical modelling of indentation-induced densification in amorphous silica." *Acta Materialia* 56.13 (2008): 3222-3228.
- [44] Kurkjian, Charles R., Gunther W. Kammlott, and M. Munawar Chaudhri. "Indentation Behavior of Soda-Lime Silica Glass, Fused Silica, and Single-Crystal Quartz at Liquid Nitrogen Temperature." *Journal of the American Ceramic Society* 78.3 (1995): 737-744.

- [45] Hertz, Heinrich. *Miscellaneous papers*. Macmillan, 1896.
- [46] Sneddon, Ian N. "The relation between load and penetration in the axisymmetric Boussinesq problem for a punch of arbitrary profile." *International journal of engineering science* 3.1 (1965): 47-57.
- [47] Tabor, David. *The hardness of metals*. Oxford university press, 2000.
- [48] Hill, Rodney. *The mathematical theory of plasticity*. Vol. 11. Oxford university press, 1998.
- [49] Johnson, K. L. *Contact Mechanics*. Cambridge University Press, 1987.
- [50] Ernsberger, F. M. "Role of densification in deformation of glasses under point loading." *Journal of the American Ceramic Society* 51.10 (1968): 545-547.
- [51] Barlet, Marina, et al. "Hardness and toughness of sodium borosilicate glasses via Vickers's indentations." *Journal of Non-Crystalline Solids* 417 (2015): 66-79.
- [52] Aakermann, Kim G., et al. "Indentation deformation mechanism of isostatically compressed mixed alkali aluminosilicate glasses." *Journal of Non-Crystalline Solids* 426 (2015): 175-183.
- [53] Oliver, Warren Carl, and George Mathews Pharr. "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments." *Journal of materials research* 7.06 (1992): 1564-1583.
- [54] Arora, A., et al. "Indentation deformation/fracture of normal and anomalous glasses." *Journal of Non-Crystalline Solids* 31.3 (1979): 415-428.
- [55] Yoshida, Satoshi, et al. "Fracture-and Indentation-Induced Structural Changes of Sodium Borosilicate Glasses." *International Journal of Applied Glass Science* 3.1 (2012): 3-13.
- [56] Yoshida, Satoshi, Jean-Christophe Sangleboëuf, and Tanguy Rouxel. "Quantitative evaluation of indentation-induced densification in glass." *Journal of materials research* 20.12 (2005): 3404-3412.
- [57] Koike, A., and M. Tomozawa. "IR investigation of density changes of silica glass and soda-lime silicate glass caused by microhardness indentation." *Journal of non-crystalline solids* 353.24 (2007): 2318-2327.
- [58] Yoshida, Satoshi, Jean-Christophe Sangleboëuf, and Tanguy Rouxel. "Quantitative evaluation of indentation-induced densification in glass." *Journal of materials research* 20.12 (2005): 3404-3412.
- [59] Keryvin, Vincent, et al. "Constitutive modeling of the densification process in silica glass under hydrostatic compression." *Acta Materialia* 62 (2014): 250-257.
- [60] Kermouche, Guillaume, et al. "Mechanical modelling of indentation-induced densification in amorphous silica." *Acta Materialia* 56.13 (2008): 3222-3228.
- [61] Lambropoulos, John C., Su Xu, and Tong Fang. "Constitutive law for the densification of fused silica, with applications in polishing and microgrinding." *Journal of the American Ceramic Society* 79.6 (1996): 1441-1452.
- [62] Molnár, Gergely, et al. "Densification dependent yield criteria for sodium silicate glasses—an atomistic simulation approach." *Acta Materialia* 111 (2016): 129-137.
- [63] Mantsi, B., et al. "Atomistic response of a model silica glass under shear and pressure." *The European Physical Journal B-Condensed Matter and Complex Systems* 85.9 (2012): 1-13.
- [64] Imaoka, M., and I. Yasui. "Finite element analysis of indentation on glass." *Journal of Non-Crystalline Solids* 22.2 (1976): 315-329.
- [65] Striepe, Simon, et al. "Elastic and micromechanical properties of isostatically compressed soda–lime–borate glasses." *Journal of Non-Crystalline Solids* 364 (2013): 44-52.

- [66] Malchow, P., et al. "Composition and cooling-rate dependence of plastic deformation, densification, and cracking in sodium borosilicate glasses during pyramidal indentation." *Journal of Non-Crystalline Solids* 419 (2015): 97-109.
- [67] Sellappan, P., et al. "Composition dependence of indentation deformation and indentation cracking in glass." *Acta Materialia* 61.16 (2013): 5949-5965.
- [68] Fischer-Cripps, A. C. "Elastic-plastic behaviour in materials loaded with a spherical indenter." *Journal of materials science* 32.3 (1997): 727-736.
- [69] Davies, R. M. "The determination of static and dynamic yield stresses using a steel ball." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 197. No. 1050. The Royal Society, 1949.
- [70] Daloz, W. L., A. A. Wereszczak, and O. M. Jadaan. "Apparent Yield Strength of Hot-Pressed SiCs." *Advances in Ceramic Armor IV: Ceramic Engineering and Science Proceedings, Volume 29, Issue 6* (2009): 107-118.
- [71] Swain, M. V., and J. T. Hagan. "Indentation plasticity and the ensuing fracture of glass." *Journal of Physics D: Applied Physics* 9.15 (1976): 2201.
- [72] Lawn, Brian R. "Indentation of ceramics with spheres: a century after Hertz." *Journal of the American Ceramic Society* 81.8 (1998): 1977-1994.
- [73] Fischer-Cripps, Anthony C., and Brian R. Lawn. "Stress Analysis of Contact Deformation in Quasi-Plastic Ceramics." *Journal of the American Ceramic Society* 79.10 (1996): 2609-2618.
- [74] Herbert, E. G., et al. "On the measurement of stress-strain curves by spherical indentation." *Thin solid films* 398 (2001): 331-335.
- [75] Cao, Yan Ping, and Jian Lu. "A new method to extract the plastic properties of metal materials from an instrumented spherical indentation loading curve." *Acta materialia* 52.13 (2004): 4023-4032.
- [76] Nayebi, A., et al. "New procedure to determine steel mechanical parameters from the spherical indentation technique." *Mechanics of Materials* 34.4 (2002): 243-254.
- [77] Zhao, Manhong, et al. "A new approach to measure the elastic-plastic properties of bulk materials using spherical indentation." *Acta Materialia* 54.1 (2006): 23-32.
- [78] Lee, Hyungyil, Jin Haeng Lee, and George M. Pharr. "A numerical approach to spherical indentation techniques for material property evaluation." *Journal of the Mechanics and Physics of Solids* 53.9 (2005): 2037-2069.
- [79] Taljat, Boštjan, Thomas Zacharia, and Franc Kosel. "New analytical procedure to determine stress-strain curve from spherical indentation data." *International Journal of Solids and Structures* 35.33 (1998): 4411-4426.
- [80] Liu, Ling, et al. "Can indentation technique measure unique elastoplastic properties?." *Journal of Materials Research* 24.3 (2009): 784-800.
- [81] Giannakopoulos, A. E., and S. Suresh. "Determination of elastoplastic properties by instrumented sharp indentation." *Scripta materialia* 40.10 (1999): 1191-1198.
- [82] Dao, M., et al. "Computational modeling of the forward and reverse problems in instrumented sharp indentation." *Acta materialia* 49.19 (2001): 3899-3918.
- [83] Swab, Jeffrey J., et al. "Knoop hardness-apparent yield stress relationship in ceramics." *International Journal of Applied Ceramic Technology* 9.3 (2012): 650-655.
- [84] Joslin, D. L., and W. C. Oliver. "A new method for analyzing data from continuous depth-sensing microindentation tests." *Journal of Materials Research* 5.1 (1990): 123-126.
- [85] Pethica, J. B., and W. C. Oliver. "Mechanical properties of nanometre volumes of material: use of the elastic response of small area indentations." *MRS Online Proceedings Library Archive* 130 (1988).
- [86] Wereszczak, Andrew A., and Charles E. Anderson Jr. "Borofloat and starphire float glasses: A comparison." *International Journal of Applied Glass Science* 5.4 (2014): 334-344.

- [87] Mesarovic, Sinisa Dj, and Norman A. Fleck. "Spherical indentation of elastic–plastic solids." *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. Vol. 455. No. 1987. The Royal Society, 1999.
- [88] Vukceovich, M. R. "A new interpretation of the anomalous properties of vitreous silica." *Journal of Non-Crystalline Solids* 11.1 (1972): 25-63.
- [89] ASTM E9-09(2018) Standard Test Methods of Compression Testing of Metallic Materials at Room Temperature, ASTM International, West Conshohocken, PA, 2018
- [90] Packard, C. E., and C. A. Schuh. "Initiation of shear bands near a stress concentration in metallic glass." *Acta Materialia* 55.16 (2007): 5348-5358.
- [91] Pan, D., et al. "Experimental characterization of shear transformation zones for plastic flow of bulk metallic glasses." *Proceedings of the National Academy of Sciences* 105.39 (2008): 14769-14772.
- [92] Nachum, S., and A. L. Greer. "Indentation size effect in metallic glasses: Mean pressure at the initiation of plastic flow." *Journal of Alloys and Compounds* 615 (2014): S98-S101.
- [93] Bahr, David F., D. E. Kramer, and W. W. Gerberich. "Non-linear deformation mechanisms during nanoindentation." *Acta materialia* 46.10 (1998): 3605-3617.
- [94] Davis, K. M., and M. Tomozawa. "Water diffusion into silica glass: structural changes in silica glass and their effect on water solubility and diffusivity." *Journal of Non-Crystalline Solids* 185.3 (1995): 203-220.
- [95] Tomozawa, Minoru. "Water in glass." *Journal of Non-Crystalline Solids* 73.1-3 (1985): 197-204.
- [96] Ledieu, A., et al. "Leaching of borosilicate glasses. I. Experiments." *Journal of Non-Crystalline Solids* 343.1-3 (2004): 3-12.
- [97] Bunker, Bruce C., et al. "The structure of leached sodium borosilicate glass." *Physics and Chemistry of Glasses* 29.3 (1988): 106-120.
- [98] Tadjiev, Damir R., and Russell J. Hand. "Surface hydration and nanoindentation of silicate glasses." *Journal of Non-Crystalline Solids* 356.2 (2010): 102-108.
- [99] McMillan, Peter W., and A. Chlebik. "The effect of hydroxyl ion content on the mechanical and other properties of soda-lime-silica glass." *Journal of Non-Crystalline Solids* 38 (1980): 509-514.
- [100] Lawn, Brian R., T. P. Dabbs, and Carolyn J. Fairbanks. "Kinetics of shear-activated indentation crack initiation in soda-lime glass." *Journal of materials science* 18.9 (1983): 2785-2797.
- [101] Kolluru, Pavan V., et al. "Effects of surface chemistry on the nanomechanical properties of commercial float glass." *Journal of the American Ceramic Society* 93.3 (2010): 838-847.
- [102] Acocella, John, Minoru Tomozawa, and E. B. Watson. "The nature of dissolved water in sodium silicate glasses and its effect on various properties." *Journal of Non-Crystalline Solids* 65.2-3 (1984): 355-372.
- [103] Cailleateau, Céline, et al. "Insight into silicate-glass corrosion mechanisms." *Nature materials* 7.12 (2008): 978.
- [104] Bunker, B. C. "Molecular mechanisms for corrosion of silica and silicate glasses." *Journal of Non-Crystalline Solids* 179 (1994): 300-308.
- [105] Plodinec, M. J. "Borosilicate glasses for nuclear waste immobilisation." *Glass Technology* 41.6 (2000): 186-192.
- [106] Saha, Ranjana, and William D. Nix. "Effects of the substrate on the determination of thin film mechanical properties by nanoindentation." *Acta materialia* 50.1 (2002): 23-38.
- [107] Makishima, Akio, J. D. Mackenzie, and J. J. Hammel. "The leaching of phase-separated sodium borosilicate glasses." *Journal of Non-Crystalline Solids* 31.3 (1979): 377-383.

- [108] Rébiscoul, D., et al. "Water dynamics in nanoporous alteration layer coming from glass alteration: an experimental approach." *The Journal of Physical Chemistry C* 119.28 (2015): 15982-15993.
- [109] Stolper, Edward. "Water in silicate glasses: an infrared spectroscopic study." *Contributions to Mineralogy and Petrology* 81.1 (1982): 1-17.
- [110] Husung, Roy D., and Robert H. Doremus. "The infrared transmission spectra of four silicate glasses before and after exposure to water." *Journal of Materials Research* 5.10 (1990): 2209-2217.
- [111] Davis, K. M., and M. Tomozawa. "An infrared spectroscopic study of water-related species in silica glasses." *Journal of Non-Crystalline Solids* 201.3 (1996): 177-198.
- [112] Amma, Shin-ichi, et al. "Effect of glass composition on the hardness of surface layers on aluminosilicate glasses formed through reaction with strong acid." *Journal of the American Ceramic Society* 101.2 (2018): 657-665.
- [113] Bartholomew, Roger F. "Water in glass." *Treatise on materials science & technology*. Vol. 22. Elsevier, 1982. 75-127.
- [114] Cook, Lee M. "Chemical processes in glass polishing." *Journal of non-crystalline solids* 120.1-3 (1990): 152-171.
- [115] Tabor, David. "The hardness of solids." *Review of physics in technology* 1.3 (1970): 145.
- [116] El-Egili, K. "Infrared studies of Na₂O–B₂O₃–SiO₂ and Al₂O₃–Na₂O–B₂O₃–SiO₂ glasses." *Physica B: Condensed Matter* 325 (2003): 340-348.
- [117] Möncke, Doris, et al. "On the connectivity of borate tetrahedra in borate and borosilicate glasses." *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B* 56.5 (2015): 203-211.
- [118] Konijnendijk, Willem L. *The Structure of Borosilicate Glasses*. Eindhoven: Philips' Gloeilampenfabrieken, 1975. Print.
- [119] Manara, D., A. Grandjean, and D. R. Neuville. "Advances in understanding the structure of borosilicate glasses: A Raman spectroscopy study." *American Mineralogist* 94.5-6 (2009): 777-784.
- [120] Furukawa, Toshiharu, and William B. White. "Raman spectroscopic investigation of sodium borosilicate glass structure." *Journal of materials science* 16.10 (1981): 2689-2700.
- [121] Meera, B. N., and J. Ramakrishna. "Raman spectral studies of borate glasses." *Journal of Non-Crystalline Solids* 159.1-2 (1993): 1-21.
- [122] Winterstein-Beckmann, A., et al. "Raman spectroscopic study of structural changes induced by micro-indentation in low alkali borosilicate glasses." *Journal of Non-Crystalline Solids* 401 (2014): 110-114.

VITA

Benjamin L. Hackett was born on July 22, 1992 in Greensboro, NC. Soon thereafter, Benjamin found his childhood home near Athens, GA. He moved to Northern Kentucky as an adolescent and graduated from Beechwood High School in 2010. Benjamin received a bachelor's degree in materials engineering from the University of Kentucky in 2014. He moved to Knoxville, TN in the fall of 2014 to pursue graduate studies at the University of Tennessee under the tutelage of Dr. George Pharr.