Indentation deformation mechanism in glass: Densification versus shear flow

T. Rouxel,1,a) H. Ji,1 J. P. Guin,1 F. Augereau,2 and B. Ruffle3

1Applied Mechanics Laboratory of the University of Rennes 1, LARMAUR, ERL CNRS 6274, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France
2LAIN, UMR 5011, CNRS-Université Montpellier II, Place E. Bataillon, CC 082, F-3409 Montpellier cedex, France
3LCVN, UMR 5587, CNRS-Université Montpellier II, Place E. Bataillon, CC 082, F-3409 Montpellier cedex, France

(Received 15 January 2010; accepted 26 March 2010; published online 7 May 2010)

Although the characteristic time constant for viscous relaxation of glass is so large at room temperature that viscous flow would be hardly detectable, a permanent deformation can be easily achieved at ambient temperature by applying a sharp contact loading—a Vickers indenter for instance—for few seconds only. We provide direct evidence for densification and volume conservative shear flow by means of atomic force microscopy topological analysis of the indentation profile and volume on as-quenched and densified specimens (pressure up to 25 GPa). We show that both possible mechanisms contribute to different extents depending on the glass composition. A major finding is that densification predominates in glasses with relatively low atomic packing density but that shear flow relays on once densification is achieved. © 2010 American Institute of Physics. [doi:10.1063/1.3407559]

I. INTRODUCTION

Glasses are brittle materials and fail in a purely elastic manner at room temperature. Nevertheless it is possible to induce a permanent deformation using a sharp indenter. This is the way hardness—a measure of the mean contact stress for the formation of a permanent imprint—is estimated. Typical values for glass hardness range between 1 (chalcogenides) and 7 (silica-rich) GPa. These values are obviously much larger than those applied during classical mechanical testing or in service conditions and are sufficient to generate some densification in a process zone beneath the indentation. There as been a long lasting controversy about the nature of the permanent indentation deformation. Although a classical plasticity approach was first considered,1 the indentation deformation proved later to be nonvolume conservative2,3 and to exhibit a time dependence (indentation-creep) at room temperature. This calls for caution regarding the definition of plastic yield stress and the use of standard equations for elastoplasticity in the case of glasses. Densification beneath the indentation was deduced from changes in the refractive index as measured by optical interferometry and was recognized to be a general property of glasses.2,3 Nevertheless, there are observations of shear lines and pileup suggesting the occurrence of shear flow at room temperature.3–6 Densification involves a collapse of matter into a more close-packed structure and is a displacive transformation. The smaller the atomic packing density is, the larger the magnitude of the volume shrinkage.7 In the case of amorphous silica (a-SiO2), densification accounts for 80% of the indentation volume, whereas for a Zr-based metallic glass, it contributes to less than 10% of the deformation.8 On the contrary, shear flow is reconstructive. As a matter of fact shear flow results in the piling-up of matter in the vicinity of the indentation whereas densification leaves a well defined indent surrounded by a weakly distorted flat surface. Note that both mechanisms are thermally activated but the activation energy associated to the densification process was found much smaller than the one for shear flow [511 and 35–55 kJ mol–1, respectively, for a-SiO2 (Refs. 9 and 10)] and unlike densification, shear flow is not kinematically bounded. Consequently the contribution of shear flows is expected to increase rapidly with the loading time and with temperature or, for glasses with different Tg values, will tend to decrease with rising Tg at a given temperature.11

II. MATERIALS AND EXPERIMENTAL PROCEDURES

In this work, we show that there is a strong effect of the glass composition on the relative importance of each contribution and that a direct estimation is possible by means of a detailed topological analysis of the indentation site using atomic force microscopy (AFM). We compare the indentation behavior of as-quenched (pristine) and pressure-densified glasses from different chemical systems including a soda-lime-silica window glass (WG) and a Zr55Cu30Ni10Al5 bulk metallic glass (BMG), covering a wide range of Tg values (numbers in brackets, in kelvin): a-SiO2 (1463), WG (835), GeSe4 (435), and BMG (673). Some pure platinum [99.99% pure, Superpure Chemets, NJ (USA)] was also investigated as a model material with high packing density behaving in an elastoplastic manner with no volume change upon plastic deformation. Pressure-densified specimens were obtained by means of an octahedral multianvil apparatus using a Walker cell and following a procedure described elsewhere.7,12 Each run consisted in raising the load pressure of the main ram at a rate of 0.5 MPa per minute. After reach-
ing the pressure target, the specimens were maintained at high pressure for 1 h and then slowly unloaded. It is noteworthy that unlike previously reported high pressure investigation specimens did not fracture during the experiments, suggesting that the pressure device induced very little shear. These glasses were indented using a Vickers indenter (pyramidal diamond with 148.1° edge to edge apical angle) under a 50 mN load for 15 s. This load was chosen low enough to prevent against visible surface radial microcracking. Then the indentation profiles and volumes were estimated from AFM measurements using a dedicated routine described elsewhere. The elastic moduli of the densified specimens were characterized by means of Brillouin scattering spectroscopy and acoustic microscopy following experimental procedures described in Ref. The combined use of these two techniques provides accurate values for the sound wave velocities $V_L$ and $V_T$.

III. HIGH PRESSURE TREATMENT EFFECTS ON THE ELASTIC PROPERTIES

The comparison between the loading (up to 250 mN) unloading curves obtained on pristine and high pressure specimens (Fig. 1) shows significant differences in the case of pressure sensitive glasses. For instance, the penetration depth decreases from 1.53 μm for the pristine a-SiO$_2$ glass to 1.29 μm for the glass densified under 25 GPa. Correlatively, Young’s modulus increases with the densification process and hardness follows the same trend in all cases but for WG (Table I). In this latter case, for pressure above 8 GPa, a slight decrease in hardness is observed (by 7% for pressure over 20 GPa). The abrupt increase in the pile-up volume for pressure above 8 GPa indicates that the contribution of shear

### Table I. Predensification and postdensification physical and mechanical properties of the glasses (nm: not-measured).

<table>
<thead>
<tr>
<th>Glass</th>
<th>Pressure (GPa)</th>
<th>$\rho$ (kg m$^{-3}$)</th>
<th>E (GPa)</th>
<th>$\nu$</th>
<th>Hv (GPa)</th>
<th>$V^+ / V^-$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-SiO$_2$</td>
<td>0</td>
<td>2.199</td>
<td>74.5</td>
<td>0.150</td>
<td>8.35</td>
<td>17</td>
</tr>
<tr>
<td>a-SiO$_2$</td>
<td>12</td>
<td>2.262</td>
<td>75.9</td>
<td>0.149</td>
<td>8.12</td>
<td>nm</td>
</tr>
<tr>
<td>a-SiO$_2$</td>
<td>20</td>
<td>2.654</td>
<td>104.5</td>
<td>0.212</td>
<td>10.80</td>
<td>nm</td>
</tr>
<tr>
<td>a-SiO$_2$</td>
<td>25</td>
<td>2.674</td>
<td>109</td>
<td>0.252</td>
<td>11.48</td>
<td>77</td>
</tr>
<tr>
<td>WG</td>
<td>0</td>
<td>2.514</td>
<td>71.5</td>
<td>0.230</td>
<td>6.25</td>
<td>22</td>
</tr>
<tr>
<td>WG</td>
<td>8</td>
<td>2.517</td>
<td>74.8$^c$</td>
<td>nm</td>
<td>6.34</td>
<td>nm</td>
</tr>
<tr>
<td>WG</td>
<td>20</td>
<td>2.672</td>
<td>78.4</td>
<td>0.228</td>
<td>5.82</td>
<td>38</td>
</tr>
<tr>
<td>WG</td>
<td>25</td>
<td>2.672</td>
<td>77.8$^c$</td>
<td>nm</td>
<td>5.75</td>
<td>38</td>
</tr>
<tr>
<td>GeSe$_4$</td>
<td>0</td>
<td>4.337</td>
<td>14.8</td>
<td>0.286</td>
<td>1.39</td>
<td>61</td>
</tr>
<tr>
<td>GeSe$_4$</td>
<td>3</td>
<td>4.396</td>
<td>15.5$^c$</td>
<td>nm</td>
<td>1.44</td>
<td>nm</td>
</tr>
<tr>
<td>GeSe$_4$</td>
<td>25</td>
<td>4.402</td>
<td>17.1$^c$</td>
<td>nm</td>
<td>1.47</td>
<td>63</td>
</tr>
<tr>
<td>BMG</td>
<td>0</td>
<td>6.830</td>
<td>81.6</td>
<td>0.380</td>
<td>5.53</td>
<td>34</td>
</tr>
<tr>
<td>BMG</td>
<td>10</td>
<td>6.864</td>
<td>105.4$^c$</td>
<td>nm</td>
<td>5.60</td>
<td>nm</td>
</tr>
<tr>
<td>Platinum</td>
<td>0</td>
<td>21.45</td>
<td>168</td>
<td>0.380</td>
<td>0.59</td>
<td>75</td>
</tr>
</tbody>
</table>

$^a$Hydrostatic pressure applied for 1 h.

$^b$Density measured with a better than 0.001 g cm$^{-3}$ accuracy by means of a density gradient method using partially miscible heavy liquors (Ref. 7).

$^c$Reduced Young’s modulus as determined by instrumented indentation method: $E^r = E/(1-\nu^2)$.

$^d$Poisson’s ratio as calculated from the acoustic wave velocities $\nu = (V_L^2 - 2V_T^2)/(2(V_L^2 - V_T^2))$.

$^e$V$^+$ and V$^-$ are the volumes of piled-up material around the indent and of the indentation print, respectively, as measured by AFM.
flow to the indentation deformation strongly increased, as
will be discussed below. The increase is particularly signi-
ficant in the case of a-SiO$_2$: 46% and 37% increase in Young’s
modulus (E) and Vickers hardness (Hv), respectively. In
cases where E was not directly measured, the reduced
Young’s modulus [E* = E/(1−ν$^2$)] where ν is Poisson’s ratio
was derived from the unloading portion of the instrumented
indentation curves. The E* values confirm the tendency, even
for glasses with larger atomic packing densities such as chal-
cogenide and BMGs which experience minor changes under
high pressure testing. Nevertheless slight differences are ob-
served between E* and E. This is likely because the studied
glasses have significantly varying Poisson’s ratio and elastic
moduli and hence lead to different indentation deformation
mechanisms and indentation profiles, as discussed further.

Poisson’s ratio is found to increase with pressure, in agree-
ment with previous investigations on a-SiO$_2$. This reflects
an increase in the atomic packing density as well as a de-
crease in the short to medium-range ordering (larger intertet-
rahedral angle distribution, tendency to larger coordination
number for Si).

IV. THE PERMANENT DEFORMATION MECHANISMS
OF GLASS IN AMBIENT CONDITIONS

The physics of permanent deformation of glass at ambi-
ent temperature under sharp contact loading has long been
intriguing especially since glasses are regarded as model
brittle linear elastic materials. On one hand classical plastic-
ity based on dislocation mobility is not expected since
glasses lack long range structural ordering at the atomic
scale. On the other hand viscous flow at ambient temperature
would require incredibly long times to be detected on the
basis of the newtonian shear viscosity coefficient. Never-
theless densification has been evidenced and there are con-
vincing studies of shear-thinning indentation flow. Direct
evidence for both mechanisms and for the predominance of
densification below $T_g$ was recently reported in synthetic
clay which showed up as a good glass “analogue” material to
study the permanent deformation mechanisms.

The primary response of the glass to the sharp contact
loading is an almost instantaneous elastic sinking of the sur-
f ace. Assuming pure linear elasticity, the equilibrium mean
contact pressure (elastic hardness) for a rigid conical indenter
of apical angle 2$\phi$ is expressed as:

$$H_d = E/[(1−\nu^2)\tan \phi].$$

As a first approximation a Vickers indenter can be as-
similated to a cone indenter producing the same projected
surface area. This gives $\phi = 70.3^\circ$ for this equivalent cone
indenter. It follows that $H_d = 13.6, 13.5, 2.89,$ and 17.1 GPa
for a-SiO$_2$, WG, GeSe$_4$, and BMG glass, respectively. These
values are typically 2 to 3 times larger than hardness values
and are large enough to promote densification in pressure
sensitive glasses. Thus, in a secondary stage, irreversible mi-
oscopic deformation events aiming at efficiently relaxing
the contact stress by increasing the contact surface area will
initiate in a process zone near the indenter tip (Fig. 2). The
defformation mechanism is either densification in glasses
with relatively low atomic packing density, or volume con-
servative shear flow in glasses with close-packed atomic net-
work, or a combination of both in general.

In the case of densification, the depth of the affected
zone beneath the indenter ($z_d$) can be roughly estimated by
using the Boussinesq’s elastic stress field stemming from a
contact force (F), assuming densification becomes negligible
once the hydrostatic stress is smaller than the pressure $P_o$
corresponding to the onset of the densification process (from
high pressure experiments), and saturates rapidly above $P_o$
(Refs. 7 and 22)

$$z_d = [F(1+\nu)/(3\pi P_o)]^{1/2}.$$

With a contact force of 3.9 N and in the case of a-SiO$_2$
[taking $\nu = 0.15$ (pristine) to 0.252 (densified), $P_o = 8$ GPa
(Ref. 7)], then $z_d = 7.7−8.1$ μm which is in excellent agree-
ment with the value (8 μm) of the depth of the zone where
the shear index was observed for the same load in a-SiO$_2$. Raman
scattering was recently used to map the densification in a vertical
cross section through a 19.6 N Vickers indent in a-SiO$_2$. Isodensification domains were
drawn. Again the depth experimentally found for the densi-
fied zone (18 μm) is corroborated by the value for $z_d$
(17.3 μm). Besides assuming a paraboloid shape for the
isodensification domains, integration of the volume shrink-
age through the overall densified area leads to a contribu-
tion of densification to the indentation volume of ~85%, in good
agreement with previous investigations at lower loads (90% in
Ref. 8). Interestingly once a-SiO$_2$ is densified $\nu$ increases
(from 0.15 to 0.25) and piling-up is observed (Figs. 3 and 4).

The dramatic increase in $V^+ / V^−$ ratio from 17% to 77%
shows that shear flow accounts for most of the deformation
and to a greater extent than in the case of GeSe$_4$ and BMG,
although there is almost no room for the densification con-
tribution in BMG. Our topological characterization (Table
I, Fig. 4) also shows that shear flow is more important in
densified silica than in densified WG. In this latter case
$V^+ / V^−$ is limited to 38% and a decrease in hardness is ob-
served after treatments under pressure over 20 GPa. A tenta-
itive explanation is that in such glass where both densification
and shear have significant contributions, the structural
changes induced by the high pressure treatments (decrease in
the mean intertetrahedral angle for instance) and the cor-

![FIG. 2. (Color online) Schematic sketch of the indentation deformation stages. The dashed line indicates the indentation profile after unloading. Arrows indicate matter displacement. σ is the mean contact pressure.](http://jap.aip.org/jap/copyright.jsp)
In the same experimental conditions 25 GPa hydrostatic pressure, 75% for BMG GeSe4, and pure platinum, respectively. The disappearance of the Hertzian cone crack and the raise of a pile-up of matter after pressure treatment.

Responding increase in Poisson’s ratio favors shear to such an extent that the glass appears slightly softer than before densification. In a previous study, it was found that for pristine silica glass, the refractive index of the glass immediately surrounding the indentation is different from that of the bulk. Therefore, it is suggested that once densification is achieved, shear flows rely on and the densified zone is partially squeezed-out toward the surface where it piles-up. Nevertheless, in cases where volume conservative flow is the dominant mechanism the pile-up volume remains noticeably smaller than the indentation volume: \( V^+ / V^- = 34\% \), 61\%, and 75\% for BMG GeSe4, and pure platinum, respectively. The case of pure platinum (polycrystalline), which is discussed here for comparison, demonstrates that even for a dense material behaving purely plastic \( V^+ < V^- \). This is because a significant fraction of material has been moved downwards in the bulk where it is responsible for postunloading residual stresses. The residual elastic stress field prevents against a complete recovery of the elastic energy stored during the loading stage and is responsible for the radial-median cracks observed at higher loads in brittle solids. It is noteworthy that the \( V^+/V^- \) values are in good agreement with those reported for synthetic clay below \( T_g \) \( V^+/V^- = 13\% \), i.e., in a range where the material contains a significant fraction of porosity, and above \( T_g \) \( V^+/V^- = 65\% \) where deformation mainly proceeds by means of a volume conservative shear process. Although indentation volume measurements were not carried out for all specimens, the fact that a relatively well defined pressure threshold exists for the onset of the densification process, located at around 3 GPa for GeSe4 and 10 GPa for both WG and a-SiO2, with a saturation at 20 GPa for the two latter glasses, suggests very similar results for GeSe4 at 3 GPa, for WG at 8 GPa, and for a-SiO2 at 12 and 20 GPa, than for the same glasses at 0 GPa, 0 GPa, 0 GPa, and 25 GPa, respectively.

Regarding the shear flow mechanism it was reported that this process is relatively more thermally activated than densification (approximately one order of magnitude difference for the activation energies) so that shear flow takes over densification at temperature from near—and above—\( T_g \) but is much reduced and perhaps nonexistent at low temperature. Having relatively low \( T_g \) temperatures, chalco-gende and to a lesser extent BMGs are potential candidates for this mechanism. Extrapolation of the viscosity curves to 293 K would give values between 1020 and 1030 Pa s. With these values and assuming a linear elasto-viscous behavior with a Newtonian viscous flow, durations of the order of thousand years would be predicted to reach the actual hardness values measured at ambient temperature after 15 s loading time. The time-dependence of hardness writes

\[
H(t) = \mu/[(1 - \nu)(1 + t/\tau) \tan \phi],
\]

where \( \tau = \eta/\mu \) is the characteristic relaxation time and \( \mu \) is the shear modulus. Note that this expression reduces to Eq. (1) for purely elastic materials (\( \eta \rightarrow \infty \)). However, both viscosity measurements and numerical simulation provide evidence for a sharp viscosity drop at high stress or strain-rate levels. This is called shear-thinning and is favored in weakly polymerized network structures. Although a description of the indentation problem in the light of nonlinear flow is far beyond the scope of this paper, it is anticipated that for shear stresses in the gigapascal order viscosity may drop of orders of magnitude. The piling-up of matter is representative of the volume conservative shear flow process. It has been extensively reported for crystals. The contribution of shear flow becomes larger than 20% of the indentation print in glasses with Poisson’s ratio over 0.25 (60% for GeSe4). Note that in GeSe4 the indentation testing duration is too small to allow for viscous flow so that most of the elastic energy stored upon loading is released during unloading. The differences observed between glasses with different Poisson’s ratio are also observed in a given chemical system by
varying the composition. For instance, in chalcogenide glasses an increase in the mean coordination number (up to 2.4 corresponding to the percolation threshold), which is associated with a decrease in \( \nu \), results in a decrease in the pile-up height. The incidence of Poisson’s ratio stems from the fact that although \( \nu \) is defined for small strain elastic perturbations only it is correlated with the packing density (open structures exhibit low \( \nu \) values and can be densified, whereas materials with \( \nu = 1/2 \) are incompressible and solely deform by means of shear processes).

V. CONCLUSION

In conclusion, this study of the indentation deformation process in glass shows that densification predominates over shear flow in glasses with relatively low atomic packing density. However, after very high pressure cycles (over 10 GPa), deformation chiefly proceeds by means of volume conservative shear flow, even in the case of a-SiO₂. Besides, Poisson’s ratio \( (\nu) \) shows up as a remarkable index to discriminate between both mechanisms. A major finding is that the shear flow contribution is higher in densified a-SiO₂ than in densified WG although it is very limited and perhaps nonexistent in the pristine glass. In contrast to crystalline materials and especially metals, for which hardness number is a measure of the shear stress required to initiate plastic flow, hardness of a glass as determined with a sharp indenter can be defined either as the resistance of a material to densification in the case of low \( \nu \), as a resistance to volume conservative shear flow (high \( \nu \) glasses), or as the combination of both in the general case.

ACKNOWLEDGMENTS

The authors are grateful to Professor Y. Kawamura from Kumamoto University (Japan) and to the LVC team of the UMR-CNRS 6226 (Rennes, France) for providing, respectively, the BMG and the GeSe₄ glass specimens. Funding for this project was provided by the Ministry of Research and Higher Education (Grant No. HJ130876-1207).