Prediction of Glass Hardness Using Temperature-Dependent Constraint Theory

Morten M. Smedskjaer,[1] John C. Mauro,[2,*] and Yuanzheng Yue[1,*]
[1]Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark
[2]Science and Technology Division, Corning Incorporated, Corning, New York 14831, USA

(Received 12 July 2010; published 8 September 2010)

Understanding the composition dependence of glass hardness is of critical importance for both advanced glass applications and for revealing underlying fracture mechanisms. We present a topological approach for quantitative prediction of hardness in multicomponent glassy systems. We show that hardness is governed by the number of network constraints at room temperature and that a critical number of constraints is required for a material to display mechanical resistance. Applied to a series of soda lime borate glasses, the predicted values of hardness are in excellent agreement with experimental measurements. Our approach is generally applicable to any network glass and demonstrates the importance of accounting for the temperature dependence of the network constraints.

DOI: 10.1103/PhysRevLett.105.115503 PACS numbers: 62.20.Qp, 65.60.+a

Hardness is an important mechanical property of materials that is defined as the resistance of a solid object to permanent deformation under pressure. The prediction of hardness has attracted much interest [1–5] since it enables a tailoring of material chemistry to yield enhanced mechanical properties. For example, the hardness of glass is a crucial issue in the development of scratch-resistant glass covers for personal electronic devices. However, direct calculation of hardness from first principles has shown to be too complex. To circumvent this problem, scientists have sought materials with large bulk or shear moduli as a surrogate for hardness [1,6], since these properties can be evaluated directly by first principles [7]. However, there is an intrinsic difference in scaling between hardness and the bulk and shear moduli, so these previous efforts have not been successful at predicting the composition dependence of hardness. For example, the bulk modulus of HfN is as high as 422 GPa, close to that of diamond (443 GPa), but its hardness is only 17 GPa in contrast to diamond's hardness of 96 GPa [6]. Recently, Gao and coworkers have successfully developed a semiempirical method for calculating the hardness of crystals by considering the strength of each individual bond and the bond density [3]. Although good agreement between calculated and measured values has been obtained for various crystalline materials [8–10], the method cannot be applied to glasses due to their high degree of structural and topological disorder. Therefore, clarifying the physical nature of hardness and enabling its quantitative prediction in glasses remains a challenge of the utmost importance.

Previous attempts have been made to correlate the hardness of oxide glasses (a) with the properties of its individual constituents [11–13], (b) with structural parameters such as the number of nonbridging oxygens (NBOs) [14], and (c) with the glass transition temperature T_g [14,15]. However, more detailed information about the glass network is required for accurate prediction of hardness [14]. In this Letter, we present an alternative topological approach for predicting the hardness of glass. This method is based on an extension of the pioneering theoretical work of Phillips and Thorpe [16–18], who introduced the idea of treating the atomic structure of a glass as a network of constraints. From subsequent experimental work, Varshneya and co-workers [19,20] established an empirical correlation between hardness and average coordination number in a series of chalcogenide glasses. Here we extend these previous studies by accounting for an explicit temperature dependence of the topological constraints, which enables an analytical derivation of the composition dependence of hardness. Previously the temperature-dependent constraint approach has been successfully applied to study the composition dependence of liquid-state properties such as T_g and fragility [21–23]. Here we extend the technique to the glassy state at room temperature, showing excellent quantitative agreement between predicted values of hardness and experimental measurements. The temperature dependence of constraints provides a natural explanation for the difference in scaling behavior between liquid-state properties at high temperature and glassy state properties at low temperature.

We consider the $x\mathrm{Na_2O}y\mathrm{CaO}0.01\mathrm{Fe_2O_3}(0.99-x-y)\mathrm{B_2O_3}$ glass series as an example with which to validate the model. This series contains an abundance of interesting structural and topological features such as the impact of network modifiers (Na, Ca) on boron coordination number. The preparation of these glasses is described in detail elsewhere [23]. For this study, we also prepared a B_2O_3 glass by melting H_3BO_3 at 1000 °C for 1 h. We determined the Vickers hardness (H_V) of the polished glasses by microindentation (Duramin 5, Struers). The indentations were performed at loads of 98 mN and 0.25 N for durations of 5 s. The hardness of each sample was measured at 30 widely separated locations.

The topological modeling approach involves three basic steps. First, we identify and count the number of distinct network-forming species. By distinct, we refer to either chemically distinct or chemically similar but having different short range order. The second step is to identify and count the number of constraints associated with each species. Third, the different constraints are ranked according to their relative bond strengths (i.e., constraint onset temperatures). Following our previous analysis [23], we consider the following types of constraints (Fig. 1), in order of decreasing strength: B-O and M^{NB}-O linear constraints (denoted "α" constraints, with an onset temperature of T_α), O-B-O angular constraints (β), and B-O-B angular constraints (γ). We also consider additional modifier rigidity due to clustering effects (μ). M^{NB} denotes the network modifiers that create NBOs and we consider two μ constraints per NBO-forming sodium, whereas there are zero μ constraints for calcium. There are two α constraints at each oxygen (both bridging and nonbridging), five β constraints per B^4 to form a rigid BO_4 tetrahedron, three β constraints per B^3 to keep the BO_3 unit planar, and one γ constraint at each oxygen. The modifiers that convert boron from B^3 to B^4 play a charge-compensating role only and are not considered as part of the network. Here we employ the discrete form of temperature-dependent constraint theory [21,22], in which a constraint is considered floppy at temperature above the onset temperature and rigid below this temperature.

The composition dependence of the experimentally obtained hardness is illustrated in Fig. 2. H_v increases with increasing Na_2O content up to around 25 mol % and then decreases. For $x + y < 1/3$, BO_3 units are converted into BO_4 units as the Na_2O content increases [23], which leads to a higher density of the relatively strong B-O bonds, and hence, an increase in hardness. For $x + y > 1/3$, NBOs start to form, leading to a decrease of H_V with increasing Na_2O content due to the decrease in the number of rigid bond constraints. The hardness of B_2O_3 is 4.4 ± 0.5 GPa at 0.25 N, i.e., softer than the soda lime borate glasses.

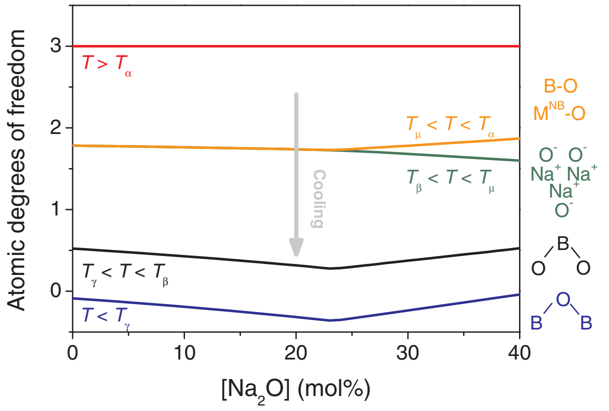

FIG. 1 (color online). Temperature (T) and composition dependence of the average number of atomic degrees of freedom in the $x\text{Na}_2\text{O}0.1\text{CaO}(0.89 - x)\text{B}_2\text{O}_3 0.01\text{Fe}_2\text{O}_3$ glasses. We have considered the following types of constraints, in order of decreasing strength (i.e., onset temperature): B-O and M^{NB}-O linear constraints (with a constraint onset temperature of T_α), O-B-O angular constraints (T_β), and B-O-B angular constraints (T_γ). As discussed elsewhere [23], we also consider additional modifier rigidity due to clustering effects around sodium (T_μ). Right panel: local atomic structures.

An interesting result is obtained by comparing the measured values of hardness and T_g (Fig. 2). H_V displays a distinct peak around the composition where the fraction of four-coordinated boron achieves a maximum, whereas there is smaller change in T_g in the same region. It should be mentioned that the maximum in $T_g(x, y)$ does not correspond to the maximum in the fraction of four-coordinated boron. This points to the importance of including the temperature dependence of network constraints when calculating properties such as $T_g(x, y)$ and $H_V(x, y)$. At high temperatures, there is ample thermal energy to overcome the bond constraints, and hence the network is floppy. As the temperature decreases, thermal energy is reduced and more constraints become frozen in (Fig. 1). At some temperature $T_0(x, y)$ all of the floppy modes are lost. The glass transition must always occur at temperatures above this rigidity percolation temperature, i.e., $T_g(x, y) > T_0(x, y)$, and consequently the low-temperature constraints are irrelevant when calculating $T_g(x, y)$. However, since hardness is measured in the glassy state at room temperature, i.e., for $T < T_g(x, y)$, the additional low-temperature constraints are important (viz., the B-O-B angular γ constraints) and must be considered in the model.

To predict the composition dependence of glass hardness, we start from the idea that a certain critical number of constraints (n_{crit}) must be present in order to produce a connected network that is required for the material to display mechanical resistance, i.e., for hardness to become nonzero. When the average number of atomic constraints is less than this critical value ($n < n_{\text{crit}}$) the mechanical re-

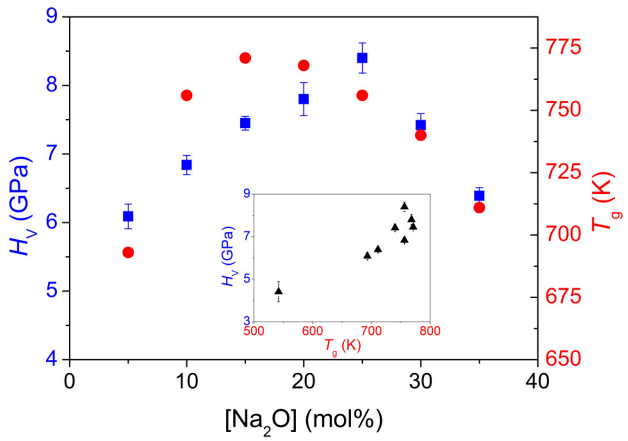

FIG. 2 (color online). Composition dependence of Vickers hardness (H_V, plotted as squares) and glass transition temperature (T_g, circles) for the $x\text{Na}_2\text{O}0.1\text{CaO}(0.89 - x)\text{B}_2\text{O}_3 0.01\text{Fe}_2\text{O}_3$ glasses. Inset: Correlation between H_V and T_g, including the data of the B_2O_3 glass. The T_g data points of the soda lime borate glasses are taken from Ref. [23].

sponse is liquidlike, i.e., there is no resistance to an incoming indenter, and hence no hardness. When $n > n_{\text{crit}}$ there are enough constraints to make a rigid network that produces a solidlike mechanical response. A value of $n = 2$ gives a network that is rigid along one dimension (i.e., rigid chains, as in Se), whereas $n = 3$ gives a network that is rigid in three dimensions (fully isostatic). Graphite is an example of a rigid 2D structure that has very weak interactions in the third dimension to hold the layers together, i.e., its n value should be slightly larger than 2.5. The hardness of graphite is about 0.3 GPa [24], which is less than 5% of the hardness of the borate glasses, even though the bond strength of the individual C-C bonds in graphite are stronger than those in diamond. The strength of the layer-locking bond constraints in the third dimension must therefore play a decisive role for hardness. We propose that for a network to display mechanical resistance, it must be rigid in at least two dimensions. Thus, we set $n_{\text{crit}} = 2.5$ since this gives a network that is rigid in two dimensions of the three-dimensional space. In other words, rigidity in only one or two dimensions is not sufficient to resist the applied stress during the hardness measurement. Finite values of hardness are a result of the additional constraints to form a three-dimensional network. We then assume that hardness is directly proportional to the number of these additional constraints, i.e., the constraints in excess of n_{crit}. It should be emphasized that n_{crit} does not correspond to the standard three-dimensional rigidity percolation threshold, which occurs at an average coordination number of $\langle r \rangle = 2.4$ for chalcogenide systems [18] when all linear and angular bond constraints are assumed to be intact. Here we do not express n_{crit} in terms of an average coordination number since the model is developed in finer detail, treating each network-forming species and bond constraint individually rather than in an average sense.

For our specific model of the soda lime borate glasses, we calculate the average number of atomic constraints at *room temperature* (i.e., $T < T_\gamma$) by extending our previous analysis [23] to low temperatures (where all the bond-bending forces are intact). For convenience of calculation all the stretching constraints can be assigned to O, and application of the $(2\langle r \rangle - 3)$ rule [16] for calculating bond-bending constraints yields

$$n(x, y) = 5N(\mathrm{B}^4) + 3N(\mathrm{B}^3) + 3N(\mathrm{O}) + \frac{4x}{2x + y} N(M^{\mathrm{NB}}), \tag{1}$$

where $N(\mathrm{B}^4)$, $N(\mathrm{B}^3)$, $N(\mathrm{O})$, and $N(M^{\mathrm{NB}})$ are the fractions of four-coordinated boron, three-coordinated boron, oxygen (including both bridging and nonbridging varieties), and network modifiers (Na and Ca) that create nonbridging oxygens, respectively, and the last term represents the μ constraints. We predict the hardness of the soda lime borate glasses by

$$\begin{aligned} H_V(x, y) &= \left(\frac{dH_V}{dn}\right)[n(x, y) - n_{\text{crit}}] \\ &= \left(\frac{dH_V}{dn}\right)[n(x, y) - 2.5]. \end{aligned} \tag{2}$$

With this model, we find excellent agreement between the predicted and measured values of hardness, as shown in Fig. 3. Here the proportionality constant (dH_V/dn) is determined empirically and found to be dependent on the load of the indenter. It should also be noted that the hardness of pure $\mathrm{B_2O_3}$ is over-predicted by the model. This is likely due to the higher water content in the $\mathrm{B_2O_3}$ glass compared to the soda lime borate glasses [25], since $\mathrm{B_2O_3}$ is extremely hygroscopic and the introduction of hydroxyl groups is expected to break linear and angular constraints, an effect not included in the current model of Eq. (1).

The success of our model implies that the hardness of a glass can be quantitatively predicted from a basic knowledge about its network topology, with only an unknown proportionality constant (dH_V/dn) that depends on the load of the indenter. Constraint theory is therefore a power-

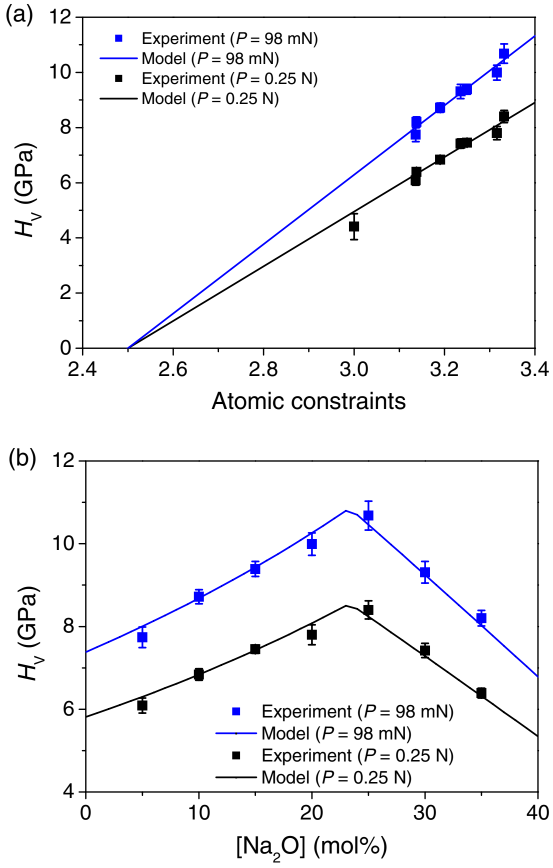

FIG. 3 (color online). Measured Vickers hardness (H_V) at loads (P) of 98 mN and 0.25 N as functions of (a) the average number of atomic constraints for $T < T_\gamma$ (i.e., at room temperature) and (b) the concentration of $\mathrm{Na_2O}$ in the soda lime borate glasses. The solid lines represent model predictions using Eq. (2) in the text with dH_V/dn equal to 12.6 and 9.9 GPa for loads of 98 mN and 0.25 N, respectively.

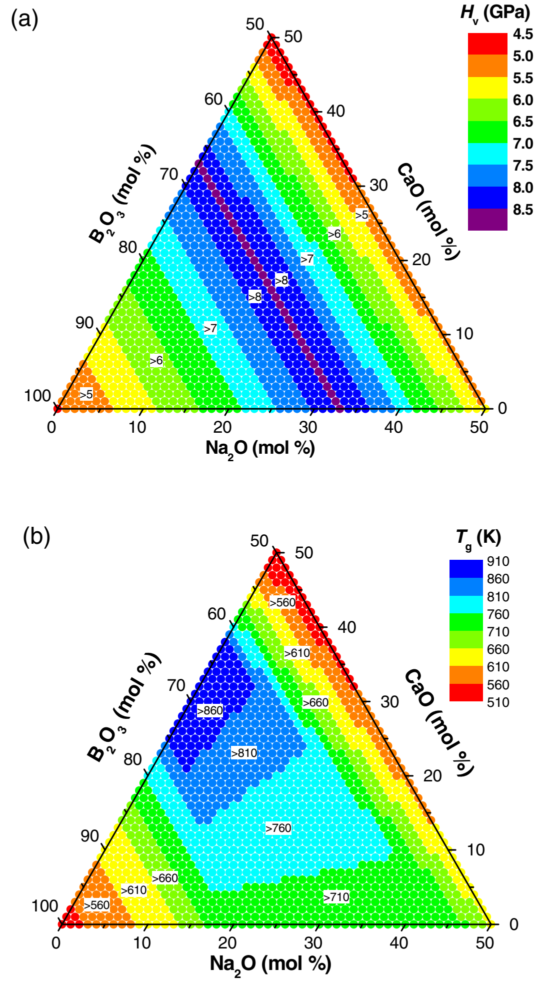

FIG. 4 (color online). Model calculations of (a) $H_V(x, y)$ at a load of 0.25 N using Eq. (1) and the model shown in Fig. 3 (black solid line) and (b) $T_g(x, y)$ [23] for the $x\mathrm{Na_2O}y\mathrm{CaO}(1-x-y)\mathrm{B_2O_3}$ system.

ful tool for efficiently exploring uncharted regions of composition space. Figure 4(a) shows a complete ternary diagram for $H_V(x, y)$ in the $x\mathrm{Na_2O}y\mathrm{CaO}(1-x-y)\mathrm{B_2O_3}$ system. Moreover, the remarkable linear relationship between room temperature constraints and hardness demonstrates the importance of considering the additional low-temperature constraints when evaluating glass properties measured at room temperature. In other words, it is crucial to account for the temperature-dependent nature of the network constraints when predicting the scaling of properties such as T_g and H_V with composition. This is illustrated by comparison of the ternary diagram for $H_V(x, y)$ [Fig. 4(a)] with that for $T_g(x, y)$ [Fig. 4(b)].

In summary, we have shown that the composition dependence of glass hardness can be accurately predicted using temperature-dependent constraint theory. A key feature of this modeling approach is that it is *analytical* and hence avoids the costly computations associated with first principles calculations. Constraint theory thus offers an efficient tool for the design of new glass compositions with desired values of properties such as hardness. The success of our approach points to the importance of accounting for the temperature dependence of the glass network constraints Our results also imply that a glass network must be rigid in at least two dimensions to have a nonzero hardness. The accurate prediction of glass hardness sheds light on the general physical nature of material hardness. The temperature-dependent constraint approach opens a new vista enabling prediction of glass hardness in multicomponent composition spaces. The compositional dependence of the proportionality constant dH_V/dn should be investigated in future work.

We greatly appreciate helpful comments from J.C. Phillips (Rutgers University) and X.J. Guo (Aalborg University). We thank Aalborg University (Ph.D. stipend No. 562/06-FS-28045) for financial support.

---

*Corresponding authors.
mauroj@corning.com.
yy@bio.aau.dk.

[1] A. Y. Liu and M. L. Cohen, Science **245**, 841 (1989).
[2] S. Veprek, J. Vac. Sci. Technol. A **17**, 2401 (1999).
[3] F. M. Gao *et al.*, Phys. Rev. Lett. **91**, 015502 (2003).
[4] A. Simunek and J. Vackar, Phys. Rev. Lett. **96**, 085501 (2006).
[5] K. Y. Li *et al.*, Phys. Rev. Lett. **100**, 235504 (2008).
[6] D. M. Teter, Mater. Res. Bull. **23**, 22 (1998).
[7] H. Yoshino and M. Mézard, Phys. Rev. Lett. **105**, 015504 (2010).
[8] J. L. He *et al.*, Phys. Rev. Lett. **94**, 015504 (2005).
[9] X. J. Guo *et al.*, J. Phys. Chem. C **111**, 13 679 (2007).
[10] M. M. Smedskjaer, M. Jensen, and Y. Z. Yue, J. Am. Ceram. Soc. **91**, 514 (2008).
[11] A. N. Georoff and C. L. Babcock, J. Am. Ceram. Soc. **56**, 97 (1973).
[12] M. Yamane and J. D. Mackenzie, J. Non-Cryst. Solids **15**, 153 (1974).
[13] R. J. Hand and D. R. Tadjiev, J. Non-Cryst. Solids (to be published).
[14] S. Deriano *et al.*, Phys. Chem. Glasses **45**, 37 (2004).
[15] J. Sehgal and S. Ito, J. Non-Cryst. Solids **253**, 126 (1999).
[16] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).
[17] J. C. Phillips and M. F. Thorpe, Solid State Commun. **53**, 699 (1985).
[18] H. He and M. F. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).
[19] D. R. Swiler, A. K. Varshneya, and R. M. Callahan, J. Non-Cryst. Solids **125**, 250 (1990).
[20] A. N. Sreeram, A. K. Varshneya, and D. R. Swiler, J. Non-Cryst. Solids **130**, 225 (1991).
[21] P. K. Gupta and J. C. Mauro, J. Chem. Phys. **130**, 094503 (2009).
[22] J. C. Mauro, P. K. Gupta, and R. J. Loucks, J. Chem. Phys. **130**, 234503 (2009).
[23] M. M. Smedskjaer *et al.*, Chem. Mater. (to be published)
[24] C.-C. Chiu, J. Mater. Sci. **27**, 3353 (1992).
[25] J. E. Shelby, Phys. Chem. Glasses **44**, 106 (2003).