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Hardness of Oxynitride Glasses: Topological Origin

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ABSTRACT: Oxynitride glasses are mixed-anion systems, in which the 2-fold coordinated oxygen atoms have been partially substituted by 3-fold coordinated nitrogen atoms. This so-called nitridation process introduces additional bonds and thereby constrains and compacts the glass network and consequently alters the glass hardness. To explore how and why hardness varies with the degree of nitridation, we have derived a topological model of oxynitride glass hardness using temperature-dependent constraint theory, by which the scaling of glass hardness with nitrogen content can be predicted. A linear model has been derived based on the assumption that the substitution of oxygen atoms with nitrogen atoms is responsible for the hardness increase due to the increase in the number (n) of bond-bending and bond-angular constraints. It turns out that the model agrees with the experimental observation, i.e., an approximate positive linear trend of the hardness change with nitrogen content is observed for a wide range of glass compositions. The topological model may thus be useful for designing new oxynitride glass compositions with targeted hardness values.
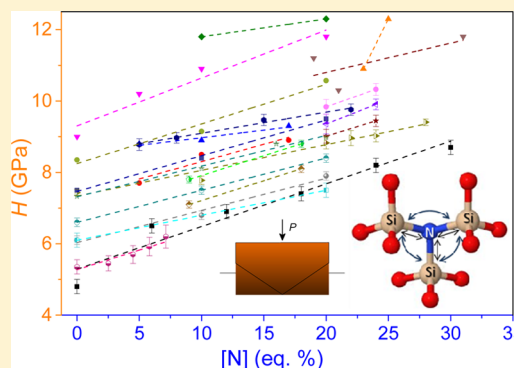
INTRODUCTION

The main drawback of glass limiting its application as a structural material is arguably its brittle fracture behavior, where the fracture process is largely governed by stress amplification at surface defects.[1] Hence, there is a need to develop stronger, that is, more damage-resistant glassy materials. Oxynitride glasses, in which the 2-fold coordinated oxygen atoms have been partially substituted by 3-fold coordinated nitrogen atoms, are of interest in this respect.[2,3] These glassy materials were first observed as grain-boundary phases in silicon-nitride based ceramics; now their potential applications include use as passive coatings on electronic substrates,[4] high-speed hard disk drive substrates,[5] bioglasses,[6] solid-state lithium batteries,[7] improved ballistic resistance for transparent armor materials,[8] and host material for LED phosphors.[9] Partial exchange of the 2-fold coordinated oxygen atoms with the 3-fold coordinated nitrogen atoms results in a greater degree of cross-linking of the anion sub-network of the glass.[10,11] This increase of the degree of the network cross-linking, along with the more covalent nature of the nitrogen-modifier cation bonding, contracts[12] and rigidifies the glass network.[13] While the Si–O single bond strength (~452 kJ/mol) is somewhat higher than that of the Si–N bond (355 kJ/mol), the increase in local bond density results in a net increase of local bond energy, what is best visible in the associated increase in Young's modulus.

Numerous investigations performed on a wide variety of oxynitride glass compositions have sought to unravel the effect of nitrogen-for-oxygen substitution on glass properties. Generally, the oxynitride glass properties are found to evolve approximately linearly with the nitrogen content, i.e., glass transition temperature, hardness, crystallization temperature, viscosity, elastic moduli, density, and refractive index increase, while the coefficient of thermal expansion decreases with increasing N/O ratio.[10,14−17] However, this phenomenological observation is possibly a result of the relatively narrow compositional range of N−O exchange which has been examined thus far. The compositional ramifications are more complex than simply a linear effect of the presence of nitrogen.[12] Consequently, the chemical composition of the base glass (e.g., nature, proportion, and interaction potential of the network-modifying cations) also influences the nitrogen solubility in the glass network and, thus, the structural configuration and macroscopic properties of oxynitride glasses.[14,18,19]

Hardness is a measure of the ability of a glass to resist elastoplastic deformation, such as abrasion and scratching. Many modern glass applications require excellent scratch resistance (e.g., smartphone and tablet covers), thus making hardness an important mechanical property. The Vickers hardness test involves static indentation with a diamond tip,[20] giving rise to elastic deformation, densification, and shear flow.[21] As a noteworthy consequence, by itself, hardness is not a material property, but an experimental phenomenology. For quantitative comparison of hardness values, the indentations

should thus be performed under identical experimental conditions when considering, e.g., the indentation size effect (ISE), which gives rise to a decrease in hardness with increasing load.[22−24] Due to the complexity and the diversity of the indentation deformation processes, the physics of the glass deformation mechanism under sharp contact loading are still controversial.[25] The increase in hardness with nitridation has been ascribed to an increased degree of network compaction for rare earth−Si−Mg−O−N,[26] Ca−Si−O−N,[27] and Y−Ca−Mg−Si−Al−O−N[28] glasses. This enhancement of the network rigidity can be attributed to the bending resistance of the N−Si$_3$ unit, which is almost ten times higher than that of the O−Si$_2$ unit,[29] ensuring an increased stiffness.[30] However, to enable quantitative predictions, the key parameters governing the composition dependence of oxynitride glass hardness are yet to be explicitly defined.

In this work, we argue that the hardness of oxynitride glasses may be understood in terms of temperature-dependent constraint theory, an approach that links the topological properties of the atomic network with the macroscopic properties of the glass. Although largely simplistic, this modeling approach presents the advantage of filtering out the unnecessary details that ultimately do not affect the glass hardness; thus, it is a convenient tool to directly calculate the hardness of a glass.[31−33] Phillips and Thorpe originally developed the concept of rigidity theory[34,35] for nonoxide covalent glasses (i.e., chalcogenides) by evaluating the glass-forming ability as a function of the number of interatomic constraints per atom relative to the number of atomic degrees of freedom per atom. The concept is based on a count of the rigid two-body (radial) and three-body (angular) constraints in the glass network. The number of rigid constraints per atom is denoted n.

Each atom, unrestrained to move in a three-dimensional space within the glass network, has three translational degrees of freedom, $d = 3$. The rigidity of the network can be determined by comparing the values of n and d. For $n < d$, the network is floppy or underconstrained, while for $n > d$, the network is stressed rigid or overconstrained. The glass network is considered to be optimally constrained and isostatic at $n = d$. By introducing a temperature dependence of the bond constraints, Gupta and Mauro have extended the original Phillips-Thorpe theory to describe and predict the compositional dependence of the dynamical properties of glassy materials by using the alkali borate system as an example.[36] Later on, the temperature dependent constraint theory has also been further developed and successfully applied to predict the dynamic properties of many other glass systems such as borosilicate,[37] phosphate,[38] borophosphate,[39] and phosphosilicate[40] glass systems. It is worth noting that the theory has also been extended to predict glass hardness.[33]

In this paper, we apply the hardness model of Smedskjaer et al.[33,41] based on topological constraint theory to predict the change in hardness of oxynitride glasses with nitrogen content and thus understand at a quantitative level the effect of nitridation on glass hardness. To this end, we take advantage of literature data of oxynitride hardness for a wide range of glass systems with various compositions in terms of both network modifying and forming cations. We also present new hardness data for a series of alkaline earth aluminosilicon oxynitride glasses. For all these systems, we investigate whether the change in hardness due to partial nitridation of an oxide glass can be quantitatively predicted using only basic topological informa-

tion about the glassy network. The impact of the applied load during indentation testing is also discussed.

TOPOLOGICAL MODEL

The properties of oxynitride glasses exhibit a clear dependence on the nitrogen content, as demonstrated in numerous studies.[10,11,14−16,42] Here we derive a model to account for the effect of nitridation (i.e., N-for-O substitution) on glass hardness, i.e., only the structural role of anions. Detailed description of the topological constraint theory, on which this model is based, can be found elsewhere.[31,37] Various compositional effects (e.g., the nature and proportion of the network-modifying and -forming cations) will influence the hardness of the base oxide glass, and it is outside the scope of this work to predict the absolute values of hardness. However, as we will show, the oxynitride glass hardness increases approximately linearly with the degree of nitridation, suggesting its independence of the base oxide glass composition, and this increase in hardness can be predicted as a function of the degree of nitrogen substitution.

The number of linear two-body stretching constraints is equal to $r_i/2$, where r_i is the coordination number of the atom i, whereas the number of angular three-body bending constraints is equal to $2r_i$-3. Each constraint is associated with a given activation energy, and it can thus be intact or thermally broken, depending on the available thermal energy. In the limit of high temperature all constraints are broken by thermal activation, while they are all intact in the low temperature limit. The onset temperature of the rigid-to-floppy transition depends on the chemical nature of the specific constraint, but all of these constraints are rigid at room temperature (300 K).[31] Oxygen thus has one bond stretching and one bond bending constraint per atom, whereas nitrogen has 1.5 stretching and 3 bending constraints per atom. These differences are illustrated in Figure 1. Consequently, a one-to-one substitution of oxygen for
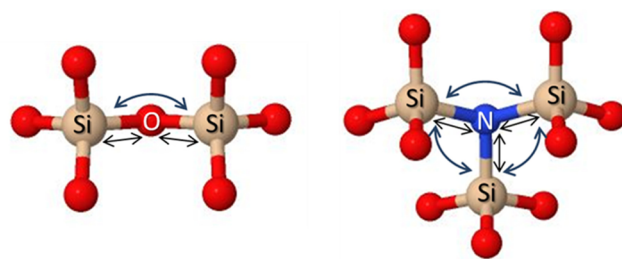
Figure 1. Illustration of two silicon tetrahedra bridged by an oxygen atom and three silicon tetrahedra bridged by a nitrogen atom. Consequently, each oxygen atom gives rise to 1 stretching and 1 bending constraints per atom, while each nitrogen atom gives rise to 1.5 stretching and 3 bending constraints per atom. The substitution of 2N-for-3O therefore increases the overall network rigidity.

nitrogen would result in a net increase of 2.5 constraints per atom. However, the difference in coordination of the two anionic species implies that the N-for-O substitution does not take place at a 1:1 atomic ratio. Instead, to maintain charge neutrality, two nitrogen atoms ($N^{3−}$) enter the network, replacing a total of three oxygen atoms ($O^{2−}$).

The relative concentrations of nitrogen and oxygen in oxynitride glasses are typically represented by expressing them in so-called equivalent units (e/o or eq.%) instead of, e.g., atomic percentage or N/O ratio. The equivalent nitrogen content is given by

$$N(e/o) = \frac{v_N[N]}{v_N[N] + v_O[O]} = \frac{3[N]}{3[N] + 2[O]} \quad (1)$$

where v_N and v_O represent the valences of nitrogen and oxygen, respectively, and [N] and [O] are their corresponding atomic concentrations. The equivalent nitrogen content is thus calculated on the basis of the ratio of charges for a given species with respect to the total amount of species with charge of the same sign. The complete N-for-O substitution (i.e., 100 eq.% N in the sub-ionic glass network) gives rise to 1 additional constraint per atom. The number of additional constraints (Δn) per atom due to nitridation can therefore be calculated as

$$\Delta n = n_N \cdot \Delta x_N - n_O \cdot \Delta x_O = \left(4.5 \cdot N(e/o) \cdot \frac{2}{3} \right.$$
$$\left. - 2 \cdot N(e/o) \cdot 1\right) = (3 \cdot N(e/o) - 2 \cdot N(e/o)) = N(e/o) \quad (2)$$

where n_N and n_O are the number of constraints associated with each nitrogen (4.5) and oxygen (2) atom, respectively, and Δx_N and Δx_O are the changes in the contents of nitrogen and oxygen, respectively, following nitridation. Therefore, this equation takes into account the atomic exchange of 2 nitrogen atoms for 3 oxygen atoms. In other words, 2/3 of a nitrogen atom can satisfy the bonds of a single oxygen atom.

According to topological constraint theory, the composition dependence of indentation hardness (H_v) can be computed as[33]

$$H(x) = \left(\frac{dH_v}{dn}\right) \cdot [n(x) - n_{crit}] \quad (3)$$

where x is the composition variable, dH/dn is proportionality determined empirically, and n_{crit} is the critical number of constraints that must be present in order to produce a connected network that is required for the material to display mechanical resistance. The proportionality (dH/dn) has previously been found to be dependent on the load of the indenter,[33] which could reflect the strain-rate sensitivity of hardness.[24] This model predicts that hardness scales linearly with the number of room temperature constraints. Here, we do not calculate the absolute values of hardness using eq 3 but rather the increase in hardness due to nitridation (ΔH) via the number of additional constraints (Δn) from eq 2:

$$\Delta H = \left(\frac{dH}{dn}\right) \cdot \Delta n = \left(\frac{dH}{dn}\right) \cdot N(e/o) \quad (4)$$

Hence, hardness is expected to increase linearly with the equivalent nitrogen concentration in the oxynitride glass, and the magnitude of this change can be predicted using eq 4 given that the proportionality constant is known. Deviations from linearity, on the other hand, could be indicative of more complex structural rearrangements with anion exchange, such as, most importantly, variations in the modifier sub-network.[38,43] The model will, in the following, be tested against experimental measurements for various oxynitride glass systems.

■ EXPERIMENTAL SECTION

Three series of alkaline earth aluminosilicon oxynitride glasses were prepared with $[SiO_2]/[Al_2O_3]$ and $[RO]-[Al_2O_3]$ values ranging from 1.6 to 2.9 and −2.9 to 8.9 mol %, respectively, where [RO] represents the total content of alkaline earth

oxides. This was done by mixing and heating the appropriate raw materials in quartz crucibles at 1650 °C for 2 h. The glasses were cooled from the melts by roller quenching. The raw materials used consisted of sand, alumina, magnesium oxide, calcium hydroxide, and aluminum nitride as nitrogen source. Composition analysis of the glasses was performed via microprobe. Electron microprobe analyses (EMPA) were performed on a JEOL 8500F instrument operated at 12 kV and 30 nA. The nitrogen content was measured using a LDE1-type diffracting crystal as a detector for EMPA, calibrated on CVD silicon nitride standard that was carbon coated at the same time as the samples.

Glasses were then polished using a diamond paste to prepare them for hardness testing. Nanoindentation measurements of hardness were performed using an Agilent G200 nanoindenter with a diamond Berkovich tip using the continuous stiffness method. In this method, a small sinusoidal displacement signal (1 nm amplitude at 45 Hz) is superimposed on the tip as it is loaded into the specimen surface. This approach permits the continuous determination of load, depth, and contact stiffness, relying on Oliver and Pharr's approximation of the indentation contact area.[44]

■ RESULTS

We first consider the three prepared series of alkaline earth aluminosilicon oxynitride glasses, with a maximum of nitrogen content of ~22 eq.%. The three series contain different $[SiO_2]/[Al_2O_3]$ and $[RO]/[Al_2O_3]$ ratios, and in each series the N/O ratio is varied. The hardness results, as measured by nanoindentation, are shown in Figure 2 and also summarized
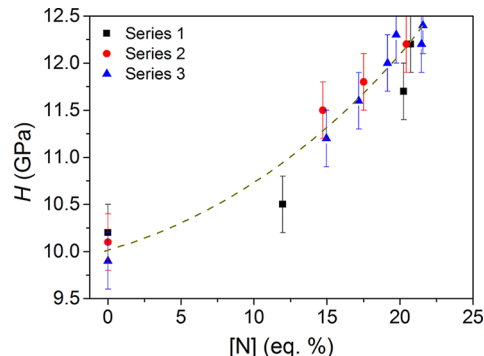
Figure 2. Dependence of hardness (H) of three series of alkaline earth aluminosilicon oxynitride glasses on the equivalent nitrogen concentration ([N] in eq.%). Series 1 has $[SiO_2]/[Al_2O_3] = 1.6$ and $[RO]-[Al_2O_3] = -2.9$ mol %. Series 2 has $[SiO_2]/[Al_2O_3] = 1.6$ and $[RO]-[Al_2O_3] = -1.8$ mol %. Series 3 has $[SiO_2]/[Al_2O_3] = 1.9$ and $[RO]-[Al_2O_3] = 8.9$ mol %. Hardness values were measured using nanoindentation. The dashed line shows the general trend for the collective data as a guide for the eye.

in Table 1. Hardness exhibits a striking positive change with the degree of nitridation in agreement with eq 4, although the data are rather scattered from the general linear trend for one of the series ($[SiO_2]/[Al_2O_3] = 1.6$; $[RO]-[Al_2O_3] = -2.9$ mol %). The base glass composition (i.e., ratio of the network formers and modifier content) does not appear to have a large impact on the oxynitride glass hardness.

We next consider hardness data for oxynitride glasses already reported in the literature, with a constant cation ratio $M^I(M^{II})$:Si:(Al) and only varying the nitrogen/oxygen ratio content. The results are shown in Figure 3 and also

Table 1. Equivalent Nitrogen Content ($N(e/o)$), Hardness (H), Coefficient of Determination (R^2) of H vs $N(e/o)$ Fit, and Proportionality Constant of Eq 4 (dH/dn) for the Three Series of Prepared Alkaline Earth Aluminosilicon Oxynitride Glasses

glass composition					
$[SiO_2]/[Al_2O_3]$ (−)	$[RO]$-$[Al_2O_3]$ (mol %)	$[N]$ (eq.%)	H (GPa)	R^2 of H vs $N(e/o)$ fit	dH/dn (GPa)
1.6	−2.9	0	10.1	0.83	8.9
		11.9	10.5		
		20.3	11.7		
		20.7	12.2		
1.6	−1.8	0	10.2	0.99	10.0
		14.7	11.5		
		17.5	11.8		
		20.4	12.2		
1.9	8.9	0	9.9	0.95	11.4
		14.9	11.2		
		19.1	12		
		21.5	12.2		
		17.2	11.6		
		19.8	12.3		
		21.5	12.4		
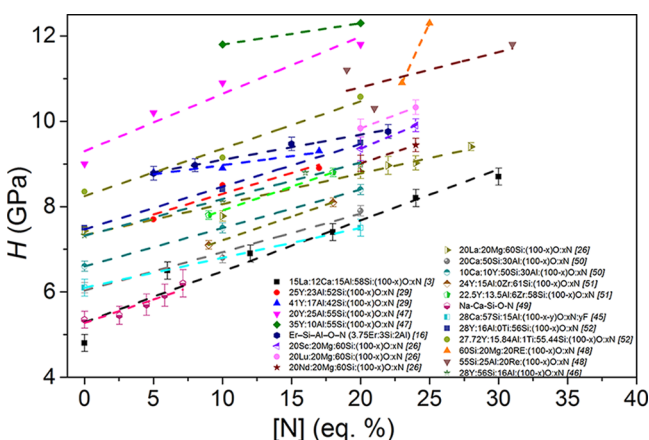
Figure 3. Dependence of hardness (H) of various oxynitride glasses on the equivalent nitrogen concentration ([N] in eq.%). Data are taken from refs 3, 16, 26, 29, and 45−52. Each series has the same base glass composition (i.e., constant cation ratio) but varying N/O ratio. The dashed lines are a guide for the eyes to show the positive trend of the change of H with [N]. Error bars are shown whenever reported in the literature.

summarized in Table 2. Most of the glasses have incorporated nitrogen content in the range of 0−24 eq.%. The hardness data were reported by various groups for relatively simple oxynitride systems, such as M−Si−(Al)−O−N, where M is the modifying cation of alkaline earth (AE)[45,46] and rare earth (RE) series[16,29,47−49] but also more complex ones with mixed cation composition, such as M^I−M^{II}−Si−(Al)−O−N, where M^I and M^{II} are modifying cation AE and RE,[3,30,46,49,50] or transition metals.[51,52] All of these data systematically show that H increases with increasing nitrogen content (or N/O ratio). Almost all of the systems thus exhibit an approximate linear evolution of hardness as a function of the equivalent nitrogen content, with an approximately constant slope (except for the two data points of the 60Si:20Mg:20RE:(100-x)O:xN system, which exhibit a steeper increase of hardness). The coefficients

of determination are in the range of $R^2 > 0.9$ (see R^2 value of linear fits in Table 2), with only the 55Si:25Al:20RE:(100-x)O:xN[49] system as a notable exception (Figure 3). However, more systematic studies are needed to test whether the linear trend is a general phenomenon for oxynitride glasses.

■ DISCUSSION

It should be noted that the hardness values of oxynitride glasses reported in the literature have been obtained through measurements conducted under different indentation conditions (e.g., type of instrument, load of the intender, time of loading, and numbers of measurement per specimen). Therefore, even glasses of similar base composition are difficult to compare due to phenomena such as the indentation size effect. This difficulty becomes even more evident when considering the following three factors. First, different nitridation methods have been applied by different authors. Second, the annealing conditions of the samples are not always described in the literature (i.e., samples may have different thermal history). Third, the noncrystalline nature of the oxynitride samples has not been confirmed for some samples (i.e., some samples may have partially crystallized). In terms of compositional changes that arise due to nitridation of the glasses, the effects of N-for-O substitution are known to be independent and additive.[26] The differences between the glasses with the same amount of nitrogen are therefore dictated by the nature of the network forming and modifying cations. However, in the following, we consider solely the effect of nitridation on glass hardness, independent of the base glass composition. The oxynitride glass systems found in the literature contain a maximum of 31 eq.% nitrogen content. Nonetheless, much higher values of incorporated nitrogen content in glassy networks have been reported, such as Ca−Si−O−N systems with 58 eq.% N[27,53] and La−Si−O−N systems with a nitrogen content up to ∼68 eq.% N,[15] although it is unclear if all these glasses are fully amorphous. In particular, such glasses have been reported to contain secondary silicide precipitates, which affect the network topology through extracting silicon species and by acting as a nanoparticulate, secondary phase, with an hitherto unknown effect on the observed hardness values. Moreover, these systems have a varying cation ratio in addition to the varying N/O ratio, and they have therefore not been considered in the present study.

As described in the Topological Model section, we consider the concept of additional constraints, Δn, as a result of the additional bonds induced by the 3-fold coordinated nitrogen atoms. It should be noted that it is possible for a fraction of the nitrogen atoms to be bridged to less than three Si atoms, leading to the presence of nonbridging nitrogen atoms.[54] Moreover, nitrogen could be incorporated in the network as N_2 or N−H. However, in this study we assume that the nitrogen is indeed cross-linking, and thus the constraints are counted equivalently, no matter whether the nitrogen atoms are bridging or nonbridging (as it is also done for the oxygen atoms). With this assumption, we calculate Δn using eq 2 for the glasses in the present study (Figure 2) and those from the literature (Figure 3). Figure 4 shows the dependence of H on Δn for all the systems. However, given the fact that the measured hardness is load-dependent[29] and the scaling factor dH/dn has previously been found to be load dependent, the data in Figure 4 has been grouped according to the applied load. Additionally, given the fact that the loads used during the indentation measurements have not been specified in the

Table 2. Range of Equivalent Nitrogen Content (N (e/o)), Coefficient of Determination (R^2) of H vs N (e/o) Fit, Applied Indentation Load (P), and Proportionality Constant of Eq 4 (dH/dn) Taken from the Literature for Various Oxynitride Glass Systems

| glass system	[N] (eq.%)	R^2 of fit	P (N)	dH/dn (GPa)	ref
15La:12Ca:15Al:85Si:(100-x)O:xN	6−30	0.94	19.6	11.9	3
41Y:17Al:42Si:(100-x)O:xN	5−17	0.95		4.3	
Y = 41%			varying		29
25Y:23Al:52Si:(100-x)O:xN	5−17	0.92	1−20	9.7	
Y = 25%					
20Y:25Al:55Si:(100-x)O:xN	0−20	0.94	nanoind	13.4	
(Al > Y)					48
35Y:10Al:55Si:(100-x)O:xN	10/20	0.99	nanoind	5.9	
(Al < Y)					
Er−Si−Al−O−N	5−22	0.99	0.98	5.9	16
20Sc:20Mg:60Si:(100-x)O:xN	20/24	0.99	4.91	13.7	
20Lu:20Mg:60Si:(100-x)O:xN	20/24	0.99	4.91	12.3	
20Nd:20Mg:60Si:(100-x)O:xN	20/24	0.99	4.91	10.8	26
20La:20Mg:60Si:(100-x)O:xN	0−28	0.97	4.91	7.4	
20Ca:50Si:30Al:(100-x)O:xN	0−20	0.98	2.94	9	
10Ca:10Y:50Si:30Al:(100-x)O:xN	0−20	0.99	2.94	9	46
24Y:15Al:61Si:(100-x)O:xN	9/18	0.99	varying	11.1	
22.5Y:13.5Al:6Zr:58Si:(100-x)O:xN	9/18	0.99	4.9−9.8	11.1	51
Na−Ca−Si−O−N	0−7.1	0.92	4.91	11.8	50
28Ca:57Si:15Al:(100-x-y)O:xN:yF	0/20	0.99	2.94	7.0	45
y = 0					
28Y:16Al:0Ti:56Si:(100-x)O:xN	0−20	0.99		10.0	
27.72Y:15.84Al:1Ti:55.44Si:(100-x)O:xN	0−20	0.95	not specified	11.1	52
20Mg:20RE: 60Si:(100-x)O:xN	23/25	0.99	nanoind	70	
RE = La^{3+}; Gd^{3+}					49
25Al:20RE:55Si:(100-x)O:xN	19−31	0.5	nanoind	8.2	
RE = La^{3+}; Gd^{3+}; Y^{3+}					
28Y: 16Al: 56Si: (100-x)O:xN	0−23	0.98	2.94	8.6	47

literature, not all of the data series present in Figure 3 have been plotted in Figure 4, in which hardness is depicted as a function of the calculated number of additional constraints due to nitridation.

The hardness values of the pure oxide glasses (i.e., for $\Delta n = 0$) depend on the base glass composition, but according to the temperature-dependent constraint model of hardness, the change in hardness due to nitridation should be independent of base glass composition and only dependent on the concentration of incorporated nitrogen. Linear regression analyses of the H vs Δn data reveals that the load-dependent proportionality constants dH/dn are within the range of approximately 5−14 GPa (see Tables 1 and 2), with the 60Si:20Mg:20RE:(100-x)O:xN[49] system being a notable exception. Disregarding this system, the average value of dH/dn is 9.9 GPa for the compositions reported in the literature and 10.1 GPa for the alkaline earth aluminosilicon oxynitride glasses prepared in this study.

These average values of dH/dn are in excellent agreement with the values found in prior studies of borate,[36] borosilicate,[37] and boroaluminosilicate[55] glasses, without any nitrogen present. For example, for borate glasses it was found that dH/dn was equal to 12.6 and 9.9 GPa for loads of 98 mN and 0.25 N, respectively. This good agreement with the previously reported values infer that the prediction model based on constraint theory is effectively validated and can be extended to quantitatively predict the hardness of oxynitride glasses using only basic topological information. Here we also find an apparent load dependence of dH/dn, especially when comparing the glasses subjected to nano- and microindentation, respectively (Figure 4). However, understanding the origin of the load dependence of dH/dn requires additional work.

■ **CONCLUSIONS**

We have analyzed literature hardness data for a wide range of oxynitride glasses and presented new results for alkaline earth
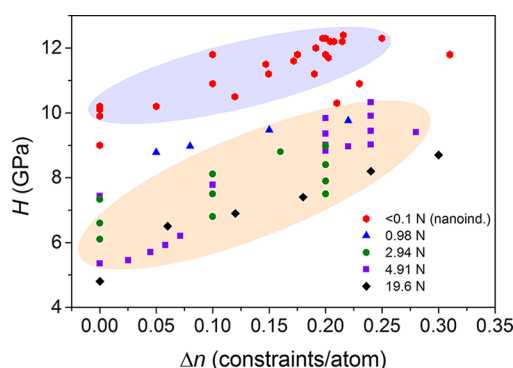
Figure 4. Hardness of various oxynitride glass systems from Figures 2 and 3 as a function of the additional number of constrains per atom (Δn) induced by the incorporation of nitrogen (eq 2). The glasses are classified according to the applied load during indentation. The shaded areas are guides for the eyes to show the trends for the groups of glasses subjected to nano- or microindentation, respectively. Some of the data shown in Figure 3 have not been plotted here due to the variation of loads used during indentation.

aluminosilicon oxynitride glasses. In general, hardness exhibits a striking positive change with the amount of nitrogen introduced into the glass network. This is the result of the introduction of additional cross-links and thus network constraints when the 3-fold coordinated nitrogen atoms are substituted for the 2-fold coordinated oxygen atoms. By deriving a topological bond constraint model of glass hardness and comparing it to the experimental data, we infer that the increase in hardness upon nitridation has a topological origin and can be quantitatively predicted by a simple enumeration of the additional room temperature bond-stretching and bond-bending constraints arising from the N-for-O substitution. The values of the load-dependent proportionality constant, dH/dn, are found to be in the same range as that reported in previous studies.

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Notes
The authors declare no competing financial interest.

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