

BOND CONSTRAINT THEORY APPLIED TO COMPLEX PHOSPHATE GLASSES



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Gutachter:

1. _____

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Tag der Verteidigung:

Dedicated to Sofia

The Road goes ever on and on
Down from the door where it began.
Now far ahead the Road has gone,
And I must follow, if I can,
Pursuing it with eager feet,
Until it joins some larger way
Where many paths and errands meet.
And whither than? I cannot say!

J. R. R. Tolkien

ABSTRACT

While the mystery of the glassy state and its fundamental relation to the glass transition temperature (T_g) is often touted as the main driving force behind research on how it depends on the glass' chemical composition, this also elicits a great deal of interest from the glass industry since the T_g is a very important parameter in virtually every modern manufacturing process. This is the background brought about the Temperature Dependent Bond Constraint Theory (TBCT) by Gupta and Mauro in 2009.

The TDBCT is based on the Bond Constraint Theory originally developed by Phillips and Thorpe to help elucidate the composition dependency of the glass forming ability of chalcogenide glasses. By abstracting the glass network as a static mechanical scaffold, they found that the glass compositions with greater glass forming ability generally are "isostatic", where the network has no excess of dangling bonds (or floppy modes – a "floppy network") and no redundant bonds (a "stressed-rigid network"), corresponding with an average coordination number of 2.4. Gupta and Mauro extended the theory by introducing the concept of temperature dependency to the constraints, which are organized in hierarchical order and become broken at certain temperatures. This allows the theory to treat the problem of the compositional dependency of the glass transition by linking the appearance of the floppy modes (or broken constraints) to the system's configurational entropy. The greatest appeal of the TDBCT is its simplicity: with just the knowledge of how the glass structure evolves with changing chemical composition one could easily model the glass transition temperature. But it also depends on several assumptions in order to be applied, some of which are stronger than others.

In order to evaluate how the TDBCT holds against closer scrutiny we based our analysis on phosphate glasses, which not only have very precise and easy to calculate evolution of the phosphate network with increasing modifier concentration, but also a plethora of reliable experimental data available in literature. This allows us to subtract the influence of the glass network from the experimental number of constraints and focus on the effect of other variables. We find that for binary phosphate glasses up until the metaphosphate composition the influence of the constraints added by the modifiers are of paramount importance to the overall behaviour of the glass. These constraints are not tied to the coordination number of the first coordination shell around the modifier, but are instead determined by the strength of the electrostatic interactions between the modifier and the surrounding non-bridging oxygens. Coupled with that, we also found that the modifier contribution depends on whether it is located in an "isolated" site (meaning that the majority of the surrounding oxygens are double-bonded to the phosphorus) or a "crosslinking" site (where the majority of the oxygens are non-bridging), and, in the case of mixed alkali ultra- and metaphosphates, whether or not one can find different modifiers in the immediate vicinity. In addition to that, experimental measurements of the glass transition temperature of silver metaphosphate – silver halide glasses are much higher than expected from

theoretical estimations; this effect is attributed to the conformation change the phosphate network goes through, transitioning from primarily chains to a mixture of chains and rings. When analyzing the viscosity and glass transition temperature of binary alkali borate glasses there are some inconsistencies that can be attributed to the glass system not complying to one of the base assumptions of the TDBCT: the average energy barrier associated with cooperative motion, represented by $B(x)$ in the Adam-Gibbs viscosity equation, is not held constant throughout the whole compositional range. The same behaviour could also be discerned in binary alkali silicate glasses, accounting for the observed severe drop on the glass transition temperature with the addition of relative small amounts of modifiers.

Finally, the outcome of the current development of the Temperature Dependent Bond Constraint Theory emphasizes its ambivalent character. On one hand, the TBCT has been shown to be a powerful model that is easy to apply and to expand, allowing it to model more complex glass compositions; on the other hand, reasonable results are only guaranteed through judiciously selecting a glass system that complies with the underlying theoretical assumptions, and the expansions to the theory highlight its empirical nature, since the additional parameters can't be calculated from first principles nor have any clear physical meaning.

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LIST OF ABBREVIATIONS

TBCT – Temperature Dependent Bond Constraint Theory

T_g – Glass transition temperature [K]

BCE – Before Common (or Current) Era

R_c – Critical cooling rate [K.s⁻¹]

S_m – Molar entropy [J.mol⁻¹.K⁻¹]

H_m – Molar enthalpy [J.mol⁻¹]

V_m – Molar volume [m³.mol⁻¹]

κ – Isothermal compressibility [m².N⁻¹]

C_p – Isobaric molar heat capacity [J.mol⁻¹.K⁻¹]

r – Coordination number of a given joint in a scaffold

n – Maxwellian number of constraints

N_c – Average number of constraints in a given network

N_d – Network dimensionality

\bar{r} – Average joint coordination number

N – Number of particles in a closed system

k – Boltzmann's constant [J.K⁻¹]

h – Planck's constant [J.s]

ω_j – Eigenfrequency of the mode j [s⁻¹]

f – Number of degrees of freedom in the network

W – Transition probability

F – Lowest free energy barrier between two neighbouring minima [J]

ν – Vibrational frequency [s⁻¹]

t – Time [s]

q – Relative degree of rigidity for a given constraint

t_{obs} – Observation time [s]

x – Compositional variable

S_c – Configurational entropy [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]

η – Viscosity [$\text{N}\cdot\text{s}\cdot\text{m}^{-2}$]

η_∞ – Viscosity at the limit of infinite temperature [$\text{N}\cdot\text{s}\cdot\text{m}^{-2}$]

B – Energy barrier for cooperative structural rearrangement [$\text{J}\cdot\text{mol}^{-1}$]

Ω – Floppy mode degeneracy

H – Heaviside step-function

CN_R – Coordination number of a given ion R

MRO – Medium range order

FSDP – First sharp diffraction peak

MAE – Mixed alkali effect

DSM – Dynamic structure model

γ – Interaction parameter between neighbouring unlike alkalis

NMR – Nuclear magnetic resonance spectroscopy

FTIR – Fourier transform infra-red spectroscopy

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1. INTRODUCTION

1.1. Glasses and the Glass Transition Temperature

Glasses are known to mankind for some 5 millennia and the first known regular production of glass vessels took place in the Asiatic Near East around 1500 BCE¹⁻⁴. These first glasses were synthesized from naturally occurring raw materials⁵ and were compositionally similar to the silicate glasses that constitute the bulk of the industrially produced glasses even nowadays. This is mainly due to the relative ease to find suitable raw materials, as silica is the most abundant oxide on Earth and its excellent glass forming ability provided by its high melt viscosity⁶. Still, during the 3000 years since their original finding, several other types of glassy materials have been discovered and invented (organic molecules, oligomers and polymers, chalcogenides, ionic and metallic), are synthesized and processed in numerous ways (melt quenching, chemical vapor deposition, polymerization, ball milling, ion sputtering) and are applied daily in a wide variety of fields, such as architecture, medicine, electronics, data transmission and storage, foodstuffs, vessels and containers, agriculture, insulation and composite materials, among many others.

The cornerstones of glass science were laid on the late 19th and early 20th century based on the works of Turner, Preston, Morey, Schott and Abbe⁷; but even today several basic questions are left without a definitive answer. A quote often cited by glass researchers comes from Nobel Prize laureate Phillip W. Anderson, who wrote in 1995 that the nature of glass and the glass transition probably is “the deepest and most interesting unsolved problem in solid-state theory”^{8,9}, and the fundamental questions of the glassy state still elicit intense discussions in the literature¹⁰⁻¹⁸. Over the years plenty of different (and sometimes conflicting) ways of defining the vitreous state have been proposed, with the most accepted description being that glasses are solids with no long range order (and therefore X-ray amorphous) and that exhibit a glass transition during heating or cooling¹⁰. The difficulty in specifying what glass is comes from its unique condition, located between liquids and solids, sharing fundamental properties from both states of condensed matter (see **Figure 1.1**). Like solids, glasses have a practically infinite viscosity, a definite shape and solid-like mechanical properties; like liquids, glasses exhibit the aforementioned lack of long range order (which is a characteristic property of crystals) and an isotropy of the properties. Such experimental results have led some to propose the vitreous state as a separate state of matter. However, as Gutzow and Schmelzer observe, similar proposals for other systems with unusual properties and structures, when compared to “classical” crystalline solids, such as gels, liquid crystals and elastomers, have been developed and not generally accepted¹¹.

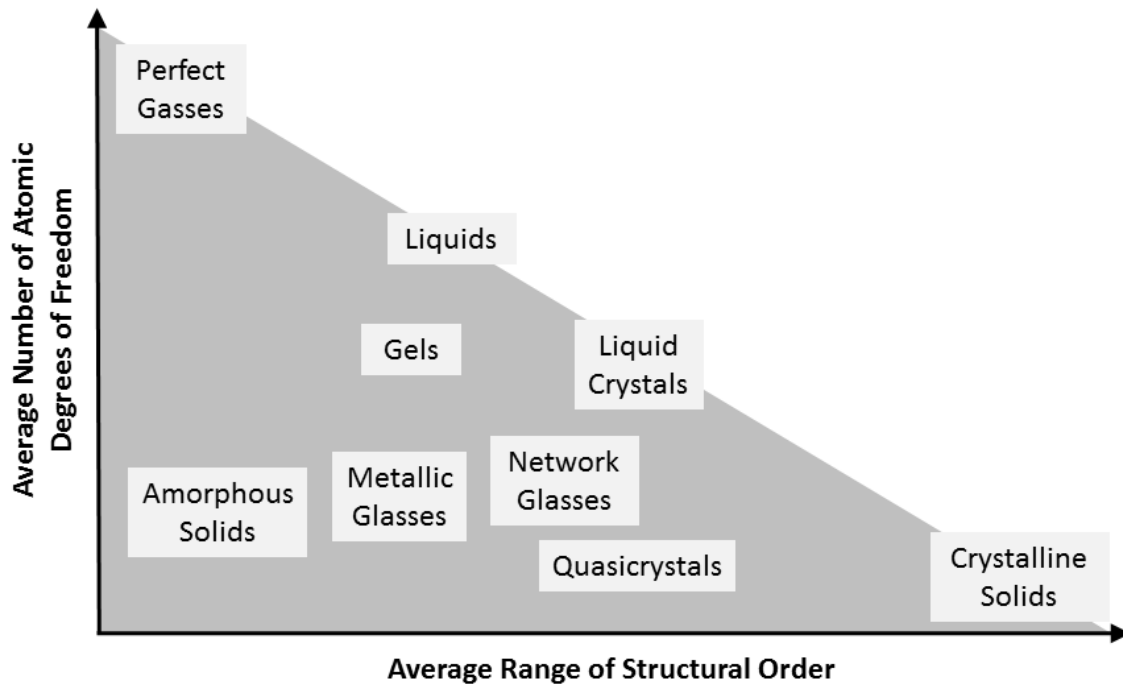


Figure 1.1. Schematic diagram showing the different aggregation states as a function of average atomic degrees of freedom and range of structural order.

Experiments show that glass formation is possible for materials belonging to all chemical types: ionic, covalent, metallic and hydrogen bonded. They can be elemental, simple chemical compounds, complex organic molecules, salt mixtures and alloys¹⁰. This wide range of materials that can be made into glasses, regardless of their particular chemical bonding and overall structure has led D. Turnbull to affirm that “all liquids would form glasses when sufficiently undercooled”¹⁹. This prediction stems from the kinetic theory of glass formation, which states that glasses are formed when the liquid (or gas) phase in question is cooled faster than a certain boundary rate (called the “critical cooling rate” – R_c) that bypasses the process of crystallization and leads to the formation of a non-crystalline solid. While it is a useful approximation for understanding the formation of glassy structures, the kinetic theory of glass formation was developed to explain glass formation in melt quenched systems. Several other processing methods circumvent totally or partially the kinetic constraints assumed by the theory, like in ball-milled glasses²⁰, sol-gel derived glasses²¹, glassy chemical deposited layers²² and thermally collapsed zeolites²³.

Even when considering just melt quenched glasses, one must not downplay the role of the structure on the glass forming ability: whereas water can be vitrified directly from the liquid, it requires extremely fast cooling rates that can only be achieved with complex experimental setups (for example see Refs.^{24,25}). Likewise, glassy alloys exhibiting predominantly metallic bonds, like Au_3Si , require very high cooling rates to achieve vitrification (between 10^5 - 10^6 K/s), while alloys containing elements with stronger covalent character (such as Pd-Ni-P or Zr-Cu-Ni bulk metallic glasses) are much better glass formers, with critical cooling rates close to 10 K/s²⁶. On the other hand, covalently bonded compounds such as silica, boron oxide, phosphorus oxide, and chalcogenides have excellent glass

forming ability as their structural units form strongly interlinked three dimensional networks; generally the addition of other chemical compounds to said glass formers (such as metallic oxides and halides to silica) leads to the disruption of the glassy network, resulting in decreased melt viscosity, enhancing the crystallization and hindering the glass formation.

Since the chemical composition and bonding parameters do not unambiguously indicate how easily any given material vitrifies, it is more useful to connect the definition of the glass state to the presence of the so-called “glass transition temperature”, as glasses share with amorphous solids the lack of long range order (even though one can still find several occurrences of the use of amorphous as a synonym for glass, these are different classes of solids¹⁵). The glass transition marks the range of temperatures where the kinetic processes characteristic of the liquid (such as diffusion, viscous flow and molecular reorientations) are greatly slowed down, leading to an exponential increase on the timescales for structural relaxation. Ultimately the constituents become unable to reach their equilibrium state during the observation, resulting on the vitrification^{27, 28}. The relation between these two timescales, the structural relaxation time and the observation time, is known as the Deborah number²⁹ and is used in statistical mechanics to distinguish systems which are in equilibrium (when the structural relaxation time is smaller than the observation time, the time averaged and ensemble averaged properties are equivalent – such systems are also referred as ergodic) or in nonequilibrium (non-ergodic systems, where the structural relaxation time is larger than the observation time and therefore the time averaged and ensemble averaged properties are not necessarily equivalent). This approach closely links the glass transition to the observation time¹⁶, so consequently it is not inherently wrong to expect that cathedral windows should flow and become thicker at the bottom; however such flow at room temperature is only expected in observation timescales larger than the age of the universe³⁰. Therefore, on experimental timescales glasses are true solids.

Unfortunately, attaching the definition of glass to the presence of the glass transition is not very helpful as there is still no universally accepted view on its dynamics or on the factors that influence the deceleration of the kinetic processes and the structural relaxation^{16, 27, 31}. It is well established that throughout the transition, first order thermodynamic parameters (molar entropy S_m , enthalpy H_m and volume V_m) show continuous change while second order parameters (molar heat capacity C_p , isothermal compressibility κ) show a sudden jump^{11, 32} (see **Figure 1.2**) and the viscosity changes abruptly. In conjunction with the observation that the glass transition temperature range is not determined solely by external thermodynamic variables (pressure P , volume V and temperature T), but is also subject to kinetic factors such as cooling (or heating) rate, observation time, and the fact that the calculated Prigogine-Defay ratio varies between 1 and 5 for multiple glass forming systems indicates that the glass transition is not a second order phase transformation.

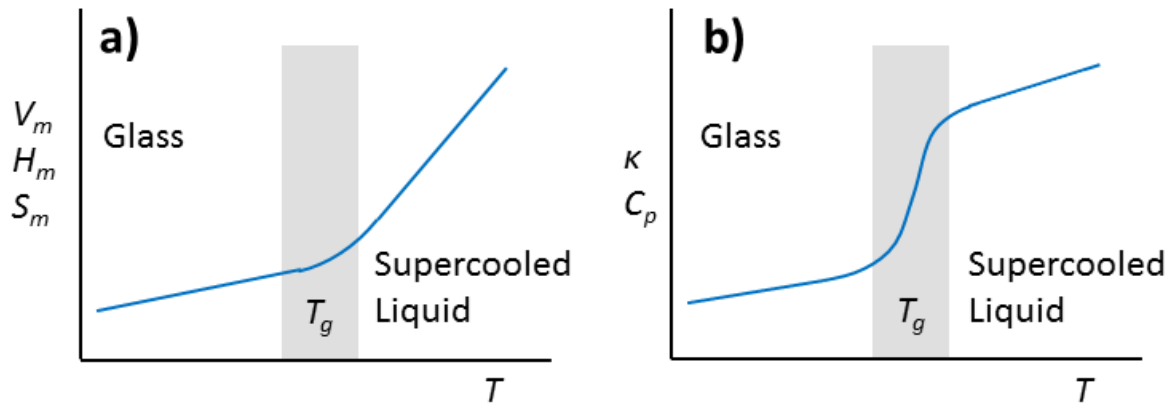


Figure 1.2. Schematic representation of the observed changes in the thermodynamic parameters as a supercooled liquid passes through the glass transition temperature. In **a)** the molar volume, enthalpy and entropy show a steady increase along the transition while in **b)** there is a sudden jump for the molar compressibility and heat capacity.

The interest in unraveling the secrets of the glass transition goes beyond scientific curiosity. A greater understanding of the dependency of the glass transition temperature on glass chemistry would facilitate the industrial development of new compositions and the improvement of existing ones since the T_g is an important processing variable informing several manufacturing steps like forming, renormalization and toughening.

1.2. Glass Network Topology and the Bond Constraint Theory

The current understanding of how glassy materials are structured have evolved significantly since the seminal works of Goldschmidt³³ and Zachariasen³⁴. Nowadays it is widely accepted that network glasses are hierarchically assembled from very defined short range units (comprising of the number of nearest neighbours and the distance), a medium range order encompassing the arrangement of the next-neighbours up to 5 interatomic distances away, and a disordered long range network^{10, 11, 15}. In the case of inorganic glasses, the chemical constituents are usually divided in two categories: “network formers” such as SiO_4 , BO_3/BO_4 and PO_4 units, referring to stable structural units with definite coordination numbers and interatomic distances due to the high covalent character of the chemical bonds; and “network modifiers”, which encompasses practically the rest of the periodic table and have much broader distributions of coordination numbers and interatomic distances due to the higher ionic character of their interactions they. However the reality is not as black and white as the network former-modifier dichotomy may lead to believe; several ions, such as Mg^{2+} , Ti^{4+} and Al^{3+} usually are classified differently in different types of glass^{35–37}, changing their role from modifiers to network formers. They appear as “intermediates” in the classifications of Dietzel³⁸, Sun³⁹ or Rawson⁴⁰. Another point of contention is the actual distribution of such species in the glassy network, where the Continuous Random Network model, heavily based on Zachariasens concepts, argues that the structural units are homogeneously and statistically distributed throughout the whole network¹⁰; while the more recent Modified Random Network model of Greaves^{41–43} proposes that the overall

distribution of structural units is heterogeneous, with the modifiers forming “channels” that surround network former rich “islands”. Regardless of what the structural units are and how homogeneously they are effectively distributed, it is widely agreed that it is this hierarchical change in structure, going from short range order to long range disorder that characterize the glassy state. Following this logic, glass compositions that are conducting to long range topological disorder should lead to glasses that are easier to synthesize.

Phillips and Thorpe^{44, 45} pioneered this topological approach to understanding how the structure of glasses can inform their properties. The glass network is abstracted as a scaffold, with atoms as connecting joints and the chemical bonds between them as joints, which allows for the calculation of its overall rigidity following the Maxwellian method⁴⁶ of counting the number of two point stretching (or linear) and three point bending (or angular) constraints associated with each structural joint. They are defined as a function of the joints coordination number r , so that its number of constraints $n(r)$ is given by (when considering only nearest neighbour central forces):

$$n(r) = \left(\frac{r}{2}\right) + (2r - 3) \quad (1.1)$$

for $r > 1$. Therefore the number of constraints in a network N_c can be easily calculated by averaging the fractions of each different type of joints present. The comparison between the values of N_c with the network dimensionality N_d is then used to classify the glass network as underconstrained (also called unbraced or floppy, for $N_c < N_d$), overconstrained (also overbraced, redundant or stressed rigid, for $N_c > N_d$), and isostatic or optimally constrained (for $N_c = N_d$)⁴⁵. Later, Gupta⁴⁷ developed a model which treats the network as composed by rigid polytopes connected by their vertices and is mathematically equivalent to the Phillips-Thorpe approach⁴⁸. In his original work, Phillips argued that optimal glass formation condition is achieved when the glass network is optimally constrained (requiring an average number of network constraints \bar{r} equal to 2.4 for a three-dimensional network), which in the chalcogenide system $\text{Ge}_x\text{Se}_{1-x}$ is found for $x = 0.2$ ⁴⁴. Further studies on ternary chalcogenides and chalcogenides have uncovered similar overall trends^{49, 50}. This behaviour has the following interpretation: when the average coordination number is smaller than 2.4, the glass network is composed of small rigid islands scattered in a unconstrained matrix, causing the melt to have very low viscosities, facilitating crystallization and inhibiting glass formation; when \bar{r} is larger than 2.4 the whole network becomes stressed due to the number of redundant constraints linking each joint, also facilitating the crystallization (for example, see Ref.⁵¹) as a mechanism to dissipate stress. In other words, the glass network is abstracted as a composite of rigid and floppy regions and as the average coordination number increases the rigid regions percolate through the network, causing a phase transition⁵².

According to Seddon⁴⁹, the calculation of \bar{r} is laden with assumptions: i) all atoms have their first neighbouring shell complete; ii) there are no voids, surfaces or non-network bonded clusters; iii) there are no large heterogeneities in the network; iv) the number of

defect sites such as dangling bonds is negligible; and v) that the chemical character of the network components is overwhelmed by the topological considerations. It is also worth mentioning that experimental suggests⁵³ that the characteristic transition at $\bar{r} = 2.4$ is not a singular, punctual shift, but two closely spaced transitions with an intermediate, topologically controlled phase situated in between. Experimental evidence for this so called “Boalchand intermediate phase” has been reported for several binary and ternary chalcogenide glasses as well as some binary silicates⁵⁴.

1.3. Temperature Dependent Constraints

As mentioned above, the assumptions implicit in the counting of constraints according to Phillips and Thorpe make it valid only for absolute zero temperature conditions. Therefore, in order to account for the effect of temperature one must use a different theoretical framework for the glass structure and discard the scaffolding analogy. One such approach is to consider the constraints that keep the scaffolding stable not as stiff bars but as energy barriers, as suggested by Goldstein⁵⁵ that atomic motions in glasses and supercooled liquids are high frequency vibrations confined in deep potential energy minima, with less frequent transitions between such minima being analogous to structural rearrangements. This concept was later developed by Stillinger and Weber⁵⁶⁻⁵⁸ into the Potential Energy Landscape formalism, which described the potential energy surface of a system comprised of N point-like particles as a function of the vector \vec{r} in $3N$ coordinates⁵⁹ (**Figure 1.3**). This vector describes the overall system at any point in time and any structural modification undergone by the structure is traced along this potential surface, in the transitions between neighbouring minima.

The energy landscape is characterized by the number, energy distribution and shape of its constitutive energy basins, defined as the set of points with steepest-descent paths leading to the same minimum, and the distribution of transition points between such basins, geometrically described as the saddle points between two adjacent basins⁶⁰. It is important to note that the energy surface is independent of the temperature; what gives rise to the dynamic effects is that at different temperatures and different time scales, different regions of the surface are able to be explored by its constituent particles^{59, 61}.

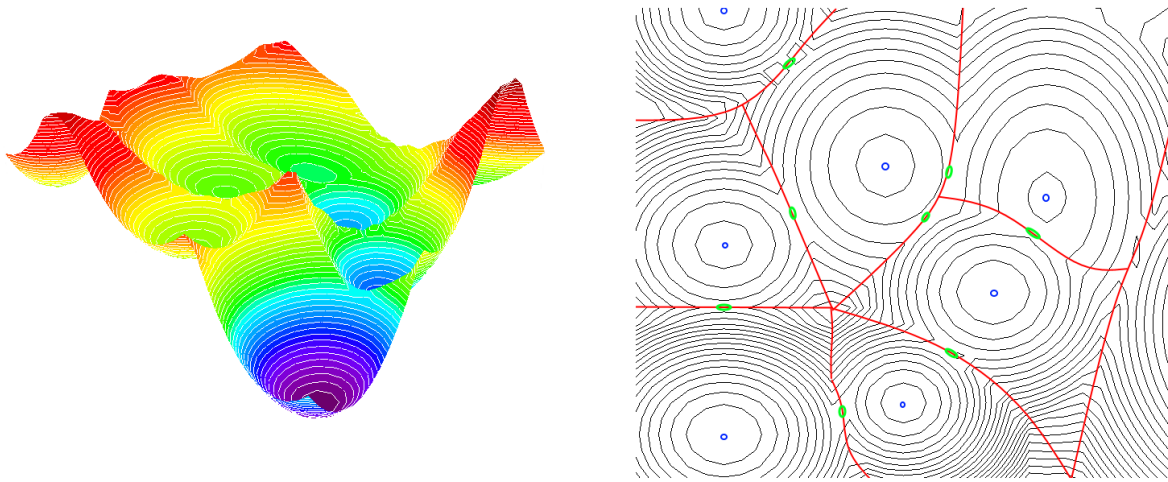


Figure 1.3. An example of a bidimensional energy landscape (**left**) and its contour plot illustrating the inherent structures of such surface (**right**). In the contour plot the red lines delimit each basin, while the blue dots show each local minimum and the green ellipses the saddle points.

According to Bowles⁶¹, a supercooled liquid passes through a transition similar to the glass transition when it becomes trapped in a particular basin because the relaxation time required to escape to neighbouring basins is comparable to the time scale of the observation, marking a transition to a non-ergodic state where the experimental time averaged ensemble is not equal to the thermal average equilibrium state^{62, 63}. From this observation, Mauro and coworkers^{64, 65} developed a computational method to calculate the glass transition temperature from first principles. However, such methods are both time and calculation intensive even for very small, chemically simple systems. One method of simplifying such calculations comes from the work developed by Naumis⁶⁶⁻⁶⁹, which correlates the configurational entropy obtained from the energy landscape (due to the geometrical shapes of its basins) with the number of floppy modes in a simple bar and hinges systems, not unlike the scaffolding model of Phillips and Thorpe, where such floppy modes of vibration create channels along the energy landscape, connecting adjacent minima and increasing the configurational entropy. Naumis arrived at the following expression⁶⁹:

$$S(T, V, N) = k \ln \left[\left(\frac{12\pi kT}{h} \right)^{3N(1-f)} \prod_{j=1}^{3N(1-f)} \left(\frac{1}{\omega_j} \right) \right] + 3Nfk \ln \left(\frac{12\pi kT}{Nh\omega_0} \right) \quad (1.2)$$

where the first term is the contribution of the number of different energy minima and the second is the channel contribution, which Naumis argues to be the controlling term. The creation of such channels throughout the energy landscape is mediated by the weakening of the chemical bonds binding the networks structural units.

Gupta and Mauro claim that such weakening can be understood as temperature dependent motion of structural units between basins, for which the transition probability W in a certain temperature and time is given by³²:

$$W(T, t) = 1 - \left[1 - \exp\left(-\frac{F}{kT}\right) \right]^{\nu} \quad (1.3)$$

where F is the lowest free energy barrier between two neighbouring basins, given by the saddle point between them and ν is the basins vibrational frequency. From this expression the relative degree of rigidity of a certain constraint $q(T)$ is defined as $1 - W(T, t_{obs})$. Therefore, when the constraint is fully broken its channel allows for all transitions ($W(T, t_{obs}) = 1 \rightarrow q(T) = 0$); likewise, if the constraint is fully intact, all transitions are blocked ($W(T, t_{obs}) = 0 \rightarrow q(T) = 1$). It is worth noting that since the constraints affect the structure, and thus the properties of the system, their degree of rigidity should depend both on the experimental observation time t_{obs} and on the relaxation time of the affected property.

The connection between this energy landscape approach and the glass transition temperature is made through the Adam-Gibbs theory⁷⁰, where the viscosity of a liquid of composition x is directly dependent on its configurational entropy $S_c(T, x)$:

$$\log \eta(T, x) = \log \eta_{\infty} + \frac{B(x)}{TS_c(T, x)} \quad (1.4)$$

where η_{∞} is the composition independent⁷¹ viscosity at infinite temperature and $B(x)$ is the energy barrier for cooperative structural rearrangement. According to Gupta and Mauro⁴⁸, since the glass transition temperature is taken as the temperature for which the viscosity is 10^{12} Pa.s independently of chemical composition, and $B(x)$ is weakly dependent of composition, then the relation between the glass transition temperature of two similar glasses of compositions x and w is only a function of the difference in their configurational entropy at T_g :

$$\frac{T_g(x)}{T_g(w)} = \frac{S_c(T_g(w), w)}{S_c(T_g(x), x)} \quad (1.5)$$

Recalling Naumis' result that the configurational entropy can be approximated as $S_c(T) = 3Nkf \ln \Omega$ (where Ω is the number of degenerate configurations per floppy mode) and that the number of floppy modes $f(T, x)$ is related to the number of constraints $n(T, x)$ by the network dimensionality N_d as $f(x) = N_d - n(x)$; substituting this into Equation 1.5 allows for the calculation of the glass transition temperature as a function of the compositional dependence of the topological constraints. One must note that this also assumes that the constraint rigidity function $q(T)$ can be approximated by a step function $q(T) = H(T_q - T)$, where T_q is the temperature above which the constraint is fully broken. Therefore calculating the number of constraints involves not only the overall geometry and connectivity of the network, but also requires the constraints to be arranged according to their relative strengths, so that only the constraints intact at T_g are considered.

Since its original publication, this approach has been used to model the compositional dependency not only of the glass transition temperature, but also surface hardness and liquid fragility of several glasses^{48, 72–85}.

1.4. Phosphate Glasses

Glasses based on P₂O₅ have been known and studied for a long time⁸⁶. While certainly not as ubiquitous as silicate and borosilicate glasses in everyday applications, mainly due to the low chemical resistance of compositions rich in phosphorus oxide, phosphate glasses are used in several specialty applications, such as soldering and sealing glasses, solid state conductors, optical and laser elements and biocompatible glasses and glass- ceramics for medicine^{87–89}. The building blocks of the phosphate glasses are the PO₄ tetrahedra^{90–93}, similarly to silicate and germanate glasses, which are based on silica and germania tetrahedra. However, unlike the aforementioned ions, the phosphorus ion has a 5⁺ charge, having only three single-bonded oxygens to bridge the structure together as one oxygen is double-bonded to the P⁵⁺ ion and therefore isolated from the glassy network^{94, 95}. As is the case in other oxide glasses, the addition of modifiers continuously decreases the network connectivity, following this general “pseudo-reaction”⁸⁷:



where n denotes the number of bridging oxygen bonds between neighbouring tetrahedra and x is the valence of the modifier R . This depolymerization is well described by the structural model developed by Hoppe⁹⁶, which also addresses a very unique characteristic of binary phosphate glasses: they can show a minimum on the glass transition temperature in the compositional range between pure vitreous phosphorus pentoxide and the associated metaphosphate. The compositional range of this minimum is found to be closely related to the coordination number of the modifier CN_R and the number of double-bonded oxygens present M_{DBO} , where $M_{DBO} = x(y+1)/y$ and y is the molar ratio of modifier oxide and phosphorus oxide in the glass composition⁹⁶. This divides the ultraphosphate compositional range ($0 < y \leq 1$) into two regions: Region I, where $M_{DBO} \geq CN_R$, the modifier ions are effectively isolated from each other, with double-bonded oxygens making up the majority of the first neighbours on the modifiers coordination shell, and increasing the modifier concentration causes a decrease on the number of bridging oxygens and, therefore, on the glass transition temperature; and Region II ($M_{DBO} < CN_R$), where there are not enough double-bonded oxygens to satisfy the first coordination shell of the modifier ions, causing the network to rearrange itself, resulting in the formation of percolating modifier rich channels between the phosphate chains (see **Figure 1.4**. Schematic representation of the two compositional regions found in ultraphosphate glasses. On Region I the number of double-bonded oxygens is larger than the coordination number of the modifier R , keeping the ions isolated; on Region II the number of double-bonded oxygens is much smaller, therefore the modifiers start sharing non-bridging oxygens in order to fulfill its first coordination shell. Figure from Ref. ⁹⁶, reproduced with

permission from the content publisher, license number 3901880515450. Copyright © 1996 published by Elsevier B.V. **Figure 1.4**), inducing the modifiers act as crosslinks between the chains, leading to an effective increase in the glass transition temperature proportional to the modifier's field strength⁹⁷⁻⁹⁹. This structural transition can be observed from the coordination number data of the modifiers as the glass composition changes: in Region I it continuously decreases with increasing modifier concentration, whereas from Region II onwards the coordination number remains relatively constant¹⁰⁰⁻¹⁰⁵.

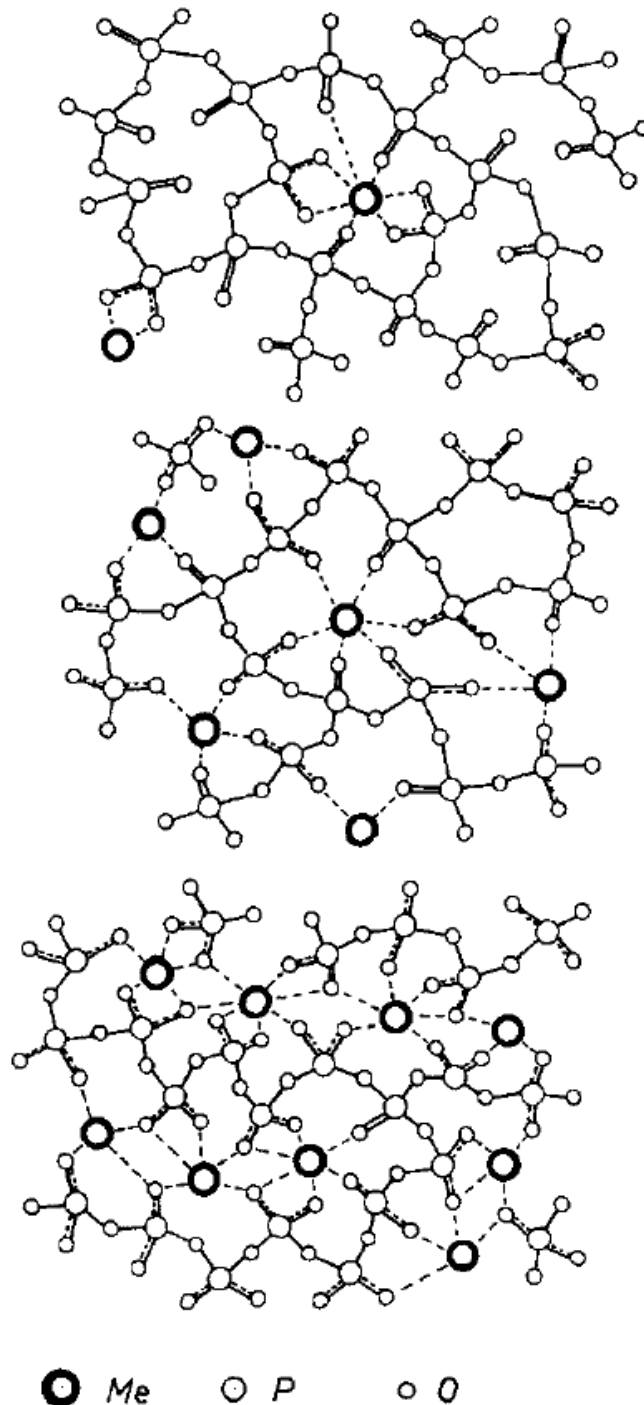


Figure 1.4. Schematic representation of the two compositional regions found in ultraphosphate glasses. On Region I the number of double-bonded oxygens is larger than the coordination number of

the modifier R, keeping the ions isolated; on Region II the number of double-bonded oxygens is much smaller, therefore the modifiers start sharing non-bridging oxygens in order to fulfill its first coordination shell. Figure from Ref. ⁹⁶, reproduced with permission from the content publisher, license number 3901880515450. Copyright © 1996 published by Elsevier B.V.

What makes the phosphate glasses, especially the binary phosphates, such an interesting system to be used as a base for extending the knowledge of bond constraints in general, as in the groundwork laid by Fu and Mauro⁷⁹, is the fact that its network forming phosphate tetrahedra bonding is reasonably analogous to the trusses and rods approximation required by the theory, the topological changes the network undergoes as the composition changes from phosphate-rich to modifier-rich glasses is very well understood, even when there are secondary effects to the depolymerization reaction, such as the disproportionation reaction $2Q^n \rightarrow Q^{n+1} + Q^{n-1}$ observed in polyphosphate and pyrophosphate compositions with modifiers of large field strength^{87, 106-113} or the effect of the modifiers on the average chain length and chain length distribution on polyphosphates^{90, 108, 114-117}. This means that the structural backbone of such glasses, especially on the case of binary alkali phosphates (and also the metaphosphates, for which there are only Q² groups making up its network regardless of the modifier ion), can be reliably and accurately modeled as the glass composition changes, allowing for a greater confidence on the correct estimation of the number of constraints acting on such glasses.

2. CUMULATIVE SUMMARY

2.1. Short Range Constraints

The Bond Constraint Theory, due to its mathematical derivation, considers on its calculations only the effects of short range constraints, meaning that only the constraints imposed on the network due to the nature and distribution of the neighbours located on the first coordination shell of the atoms that make up the glass itself. Also, the temperature dependence adopted by Gupta and Mauro⁴⁸, which forces the constraints to be either completely broken or completely intact, interpret the glass network as a rigid scaffold. Although such analogy is known to work really well for chalcogenide glasses^{48–50, 53, 66, 118, 119} because all atoms share in covalent bonds, which are both very strong and very directional. However, while such bonding can be present in oxide glasses between the so-called “network formers” and their neighbouring oxygens, these glasses also contain other elements that bond with oxygen in a much weaker¹⁰ and less directional way, characteristic of bonding with stronger ionic character. First attempts of expanding the Temperature Dependent Bond Constraint Theory to borates⁸⁵ and phosphates⁷⁹ yielded interesting results: Mauro, Gupta and Loucks’ work on lithium and sodium borates implied that the coordination environment around the modifiers is irrelevant since both glasses had similar results, but this is originated from the fact that for the compositions studied the alkali ion R^+ is “consumed” by the trigonal borate units (BO_3) to form tetragonal borate moieties ($BO_4 R^+$)^{120–124}, and therefore the modifiers do not directly interact with the network; in contrast, Fu and Mauro’s work on lithium and sodium phosphates clearly show that the theory can easily incorporate Hoppe’s structural model⁹⁶ but the assumption that both modifiers would have the same effect due to both having a coordination number of 5 (^{125, 126} *apud* ⁷⁹) leads to an overestimation of the glass transition temperature of the sodium metaphosphate by over 60 K while underestimating the glass transition of phosphate rich lithium glasses. Similarly, one can examine the example of Cs^+ and Ho^{3+} : both ions are six-fold coordinated on their respective metaphosphates^{127, 128} but show a difference of 500 K between their glass transitions⁷⁴. This effect was already noted by Eisenberg, Farb and Cool⁹⁷ in the 1960s, where they reported a linear dependence of the glass transition temperature of several phosphate glasses with the charge-to-distance ratio of the modifiers present. Trying to clarify how the Temperature Dependent Bond Constraint Theory could be extended to oxide glasses we⁷⁴ performed a comprehensive literature research of glass transition temperatures and coordination numbers for wide variety of reported metaphosphate glasses. The metaphosphate composition was selected because its network should be comprised only of Q^2 phosphate units⁹⁶, providing a stable framework with which the analysis of the modifiers effect is facilitated.

For the case of the metaphosphate glasses, we found that the relation of the glass transition temperature with the charge-to-distance ratio, as first reported by Eisenberg, Farb

and Cool⁹⁷ holds for all data available while there is no correlation between the glass transition and the modifiers coordination number⁷⁴. This suggests that the strength of the modifier constraints, as given by the number of constraints divided by its coordination number, can be different than unity and seems to depend on how strongly the short-range electrostatic interactions between the modifier and the non-bridging oxygens. Hermansen's work on similar compositions^{73, 75} proposes that such result can also be interpreted as the number of modifier constraints which are still intact. While both descriptions are mathematically equivalent, the latter interpretation is at odds with the theory's basic assumption that the constraints are either fully intact or fully broken⁴⁸. It also does not address the fact that for certain modifiers the number of intact constraints would be larger than 1 (or more than 100% of the constraints are intact), which is clearly physically impossible.

Further study on phosphates, expanding the application of the Bond Constraint Theory to the whole ultraphosphate compositional range (between pure P₂O₅ glass and the metaphosphate)⁷⁶ suggests that the modifiers are distributed in two different sites: an "isolated" site, where it is charge compensated by non-bridging oxygens of the same phosphate chain, with the remaining coordination shell comprised of double-bonded oxygens; and a "crosslinking" site, where the modifier charge is compensated by non-bridging oxygens belonging to different phosphate chains, effectively anchoring them together. Such modifier distribution is in accordance with Hoppe's structural model. It is interesting to note that, according to the experimental data, the number of constraints associated with the isolated sites is not zero, but negative values which seem to decrease with increasing ionic radius of the modifier, going from -0.90 for Li⁺ to -5.07 for Cs⁺. While it is arguable that a result of negative number of geometrical constraints is reasonable, one must consider that these numbers are not calculated from any theoretical background but are a consequence of fitting the equations to experimental data. This means that such contradictory results are likely outcome of the original equations not taking into account all the constraints which control the glass transition temperature of phosphate glasses, such as medium range order effects^{105, 110} (*e.g.* the overall distribution of voids between the phosphate chains¹²⁹) which might enable cooperative motion of small sections of the chains, with larger modifiers creating larger voids and resulting in more freedom of movement, depressing the glass transition more and yielding increasingly negative number of constraints for the isolated modifier sites.

2.1.1. Cationic Constraints effects in Metaphosphate Glasses

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Temperature-dependent bond constraint theory (BCT) relies on counting the number of atomic degrees of freedom for a given topology of a glass network. It has been proven useful as a simplistic approach towards the prediction of glass properties. However, it breaks down at the inclusion of ionic bonds and is therefore presently unable to distinguish the effects of varying cationic species with predominantly ionic bonding. Here, we consider the treatment of modifier ions in the scope of BCT. Using the example of metaphosphate glasses with a broad range of modifier cation species, we find that the theory fails to predict the glass properties because of the specific contribution of each modifier species to the rigidity of the glass network. We therefore introduce the concept of constraint strength, which is a simplistic measure of how strongly the modifiers are bound to the surrounding oxygens through columbic forces.

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Cationic constraint effects in metaphosphate glasses

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Cationic constraint effects in metaphosphate glasses

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Temperature-dependent bond constraint theory (BCT) relies on counting the number of atomic degrees of freedom for a given topology of a glass network. It has been proven useful as a simplistic approach towards the prediction of glass properties. However, it breaks down at the inclusion of ionic bonds and is therefore presently unable to distinguish the effects of varying cationic species with predominantly ionic bonding. Here, we consider the treatment of modifier ions in the scope of BCT. Using the example of metaphosphate glasses with a broad range of modifier cation species, we find that the theory fails to predict the glass properties because of the specific contribution of each modifier species to the rigidity of the glass network. We therefore introduce the concept of constraint strength, which is a simplistic measure of how strongly the modifiers are bound to the surrounding oxygens through coulombic forces. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4879559>]

I. INTRODUCTION

Bond constraint theory (BCT), as introduced by Phillips and Thorpe,^{1,2} allows for the calculation of various glass properties based on the topology of glassy networks.³ In this approach, the network topology is characterized by the average number of atomic constraints, i.e., spatial and angular invariants between constituting structural polyhedra. More recently,^{4,5} the concept of temperature-dependent constraints was introduced, based on the relation between configurational entropy and the number of topological degrees of freedom.^{6,7} This approach has been used for the calculation of the compositional dependence of the glass transition temperature and the dynamic fragility of various glass forming liquids with a remarkable degree of success.^{5,8–13}

Phosphate glasses provide a very opportune system to study the application of BCT, as there is a very good understanding of the glass structure and of how it changes with changing composition.¹⁴

For example, Fu and Mauro's study focused on BCT of binary lithium- and sodium-phosphates.¹² However, while the proposed equations managed to reproduce the overall trends of the glass transition temperature change with respect to glass composition, they were not as successful in replicating the actual T_g values. For example, according to their calculations the glass transition temperature of lithium metaphosphate and sodium metaphosphate should be around 629 K, however, an overview of the literature yields average values of 604 K for lithium metaphosphate^{15–30} and 560 K for sodium metaphosphate.^{15–24,30–37} This obvious divergence stems from the paper's assumption that both Li^+ and Na^+ are five-fold coordinated in these glasses and that according to BCT the number of constraints which any atom adds to a given system is dependent only on its first coordination shell; so in the case that two modifiers have the same coordination number, the respective binary glasses should have the exact same glass tran-

sition temperature scaling as the composition changes. This is a logical extension of BCT, as it was originally derived for chalcogenide glasses with mostly covalent bonds between its constituent atoms, which have very defined short-range environments and allow a more or less unambiguous assignment of potential degrees of freedom to a given polyhedron. However, the simple consideration of short-range interactions between the predominantly covalently bonded network formers is not sufficient to describe the properties of the glass network. For example, mid-range structural constraints⁹ such as steric hindrance and chain/ring morphology or long-range interactions induced by Coulomb forces are completely neglected in the theory's framework.

In the present report, we consider this deviation between theory and experiment which materializes in apparently over- or under-constrained compositions relative to classical BCT. We focus on the specific role of ionic constituents (cationic network modifiers) and argue that they can be treated through assigning a formal number of cationic constraints, which may increase or decrease the number of constraints predicted by classical BCT.

II. MODIFIER CONSTRAINTS

A more extreme example of the above is given by comparing Cs^+ and Ho^{3+} metaphosphates: both modifier cations are 6-fold coordinated,^{31,38} however, the glass transition temperature of CsPO_3 is around 490 K,^{15,23,24,31,39} while the T_g of $\text{Ho}(\text{PO}_3)_3$ is around 990 K,^{40,41} an astounding 500 K higher.

For a more general consideration, we fix the glass composition at the metaphosphate $\text{R}^{v+}(\text{PO}_3)_v$ (with the network modifier species R of valence v) and test for a correlation between the coordination number and the experimental glass transition temperature by varying the modifier species. This is shown in Figure 1. While there seems to be an overall trend of increasing glass transition temperature with increasing

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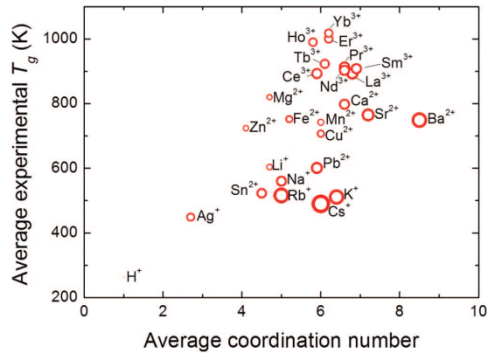


FIG. 1. Correlation of experimental glass transition temperature T_g of several metaphosphate glasses^{15-37,39-42,44-93} and the average coordination number of the modifier cation. The size of each datapoint indicates the ionic radius of the respective cation species at the specific coordination.^{31,38,72,85,90,92,94-130}

modifier coordination number, there is a considerable spread of data points, especially around the 6-fold coordination, which covers a large range of T_g values from CsPO_3 to the rare earth phosphates $\text{Ho}(\text{PO}_3)_3$, $\text{Er}(\text{PO}_3)_3$, and $\text{Yb}(\text{PO}_3)_3$. The coordination number of H^+ is assumed to be one, because calorimetric data from its phosphate glasses^{42,43} show no sign of the crosslinking effect that occurs for other modifiers, which we take as an indication that the proton is very closely bonded to a single non-bridging oxygen. This provides compelling evidence that while the contribution of the modifiers to the rigidity (or floppiness) of the network is dependent on their local environment, it cannot be determined solely by analyzing the modifiers coordination number.

In a simple approximation, the oxide coordination number of cationic modifier species may be estimated through Pauling's rules of packing, where an ideal coordination situation is obtained through geometrically dense packing of spherical ions. However, cation coordination in glassy materials is usually treated through *average coordination numbers* which are smaller than expected from Pauling's packing (Figure 2). Reasons for this deviation can be manifold, besides the general limitations of Pauling's simplistic approach. For example, the same cationic species may exist in different local environments within one glass composition. Second, coordination spheres may be strongly distorted in glasses, resulting in experimental uncertainty of the reported data on coordination numbers, especially between data which were derived through computational simulation and data which were obtained in physical experiments. The ionic radii are estimated based on the data from Shannon and Prewitt,¹³¹ where the average coordination number of an ion is used to estimate its radius.

In the context of BCT, this proves problematic, as an unambiguous value of coordination number or at least a clear distribution of coordination numbers would be required for the treatment of modifier ions. Adding to this, the prevalent ionic character of the chemical bonds between the modifiers

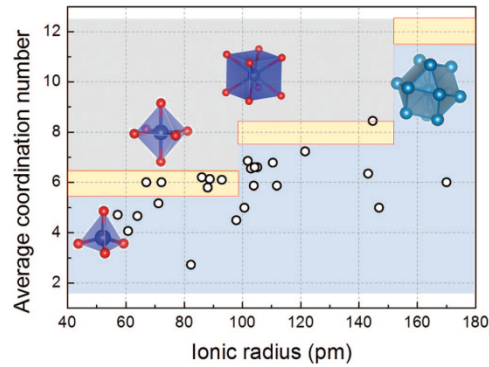


FIG. 2. Reported average coordination numbers of various modifier cations in metaphosphate glasses as a function of the calculated ionic radius. The yellow areas indicate ideal oxide coordination according to Pauling's rules of packing.

and the non-bridging oxygens compromises the applicability of the BCT since they lack the directionality and overall "rigid" geometry of covalent bonds.

In order to further investigate this problem, we calculated the number of constraints that each modifier adds to the system for several metaphosphate glasses. Fixing the glass composition at the metaphosphate allows for a very straightforward comparison between the different modifiers, since we can assume that all phosphate is present as Q^2 groups and that all modifiers have very similar environments, serving as crosslinking agents between the phosphate chains.^{14,103,132} Therefore, we can assume that for a binary phosphate glass of composition $x\text{R}_{2/v}\text{O} \cdot (1-x)\text{P}_2\text{O}_5$, where v is the ionic charge of the modifier, the number of constraints added by the modifier R at a certain composition x is expressed by

$$n_R(x) = K_R \times f_R(x), \quad (1)$$

where K_R is the number of modifier constraints per modifier and $f_R(x)$ is the fraction of modifier ions. As the number of constraints in the glass system (n_{sys}) is basically the sum of the constraints added by the network formers (n_{net}) and the modifiers, one can easily calculate the number of constraints added per modifier if experimental data on the glass transition temperature are available:

$$K_R = \frac{n_{\text{sys}}(x) - n_{\text{net}}(x)}{f_R(x)} \quad (2)$$

with $n_{\text{sys}}(x)$ given by⁴

$$n_{\text{sys}}(x) = 3 - \left[\frac{(3 - n(x_{\text{ref}}))T_g(x_{\text{ref}})}{T_g(x)} \right]. \quad (3)$$

In Eq. (3), $n(x_{\text{ref}})$ and $T_g(x_{\text{ref}})$ are the number of constraints and the glass transition temperature of the reference glass. The value of K_R is just a rescaling of the glass transition temperature, but through BCT it should correlate to the local environment of the modifier species. And exactly because

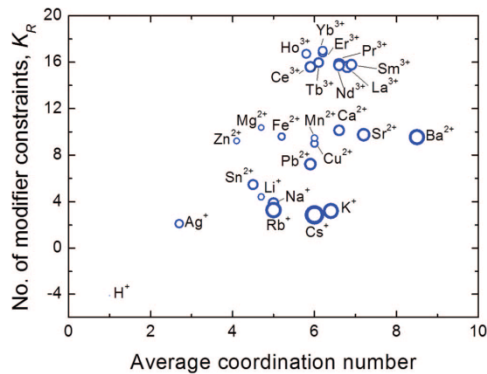


FIG. 3. Number of modifier constraints as a function of modifier average coordination number.

K_R is so strongly dependent on T_g , the data scatter seen in Figure 1 is mirrored when we try to correlate the number of modifier constraints with their coordination number (Figure 3).

Eisenberg, Farb, and Cool¹⁹ demonstrated that the glass transition temperature of some mono- and divalent binary metaphosphates strongly correlates with the intensity of the coulombic force between the modifier and the surrounding oxygens. In the context of BCT, this indicates that just the knowledge of whether a constraint (in this case, a chemical bond between the modifier and one of its first oxygen neighbours) is broken or intact is not sufficient; as already noted, one must also consider the strength of such interactions. If these interactions are controlled by electrostatic interactions than they must be proportional to the coulombic forces, which in turn are proportional to the charge-to-distance ratio¹⁹ q_R/a , where q_R is the electric charge of the modifier, in units of electron charge e , and a is the sum of the ionic radii of O^{2-} and

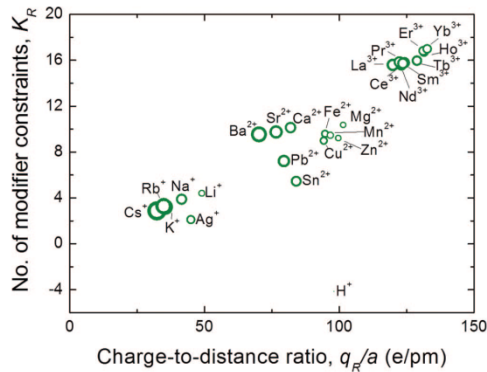


FIG. 4. Number of modifier constraints as a function of the charge-to-distance ratio for various metaphosphate glasses.

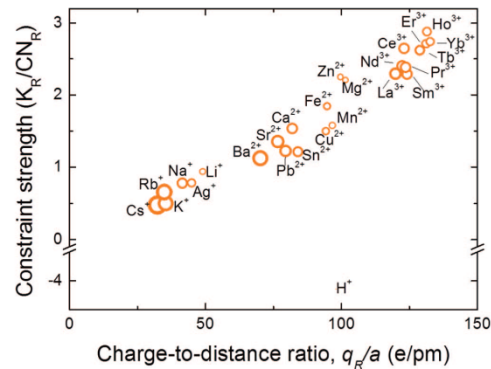


FIG. 5. Constraint strength as a function of the charge-to-distance ratio for various metaphosphate glasses.

the modifier (Figure 4). This parameter is similar to the field strength proposed by Dietzel.¹³³

The correlation which is observed in this way is remarkable. That is, the apparent number of modifier constraints correlates approximately linearly to the charge-to-distance ratio of the respective cation-oxygen pair. Only the hydrogen cation falls from this trend, what we attribute to its strong bond to only one non-bridging oxygen; as explained before, the lack of experimental evidence of the crosslinking effect in water-rich phosphoric acid glasses backs up our assessment. We take this as compelling evidence to the fact that important contributions to the modifier's constraining effect are not only due the shape or number of oxygens on its local environment, but also from the strength of the bonds between the modifier and the surrounding oxygen anions. From these data, we calculate a *constraint strength* parameter, given by the ratio of K_R/CN_R , which essentially represents how many constraints each modifier-oxygen bond adds to the system (Figure 5).

The calculated values of constraint strength show a very large distribution, ranging from 0.5 to 3 (Table I). This is in contrast to BCT, which assumes that the strength of each constraint is always unity. The reason for the observed range of cation strengths lies in the way of calculation. Here, the number of constraints has been calculated from the phosphate network. This calculation was carried-out with the implied assumption that the constraints have constraint strength of 1, effectively normalizing all further constraint strengths. Therefore, when we say that the constraint strength of Ca^{2+} is 1.54, this only applies to phosphate glasses and should be different if the glass network is based on silicate or borate units. It is interesting to notice that the constraint strength of the Li^+ ion is very close to unity while it is significantly smaller for the Na^+ ion (0.94 in comparison to 0.78), which explains why in Fu and Mauro's investigation¹² the agreement between the calculated glass transition temperature was much better for lithium phosphates than for sodium phosphates.

TABLE I. Glass transition temperatures, number of constraints per modifier, cationic potential, and modifier coordination number for several metaphosphate glasses.

R	T_g (K) ^a	K_R	Coordination number (CN_R) ^a	Charge-to-distance ratio ^b (qR/la) (e/pm)	Constraint Strength (K_R/CN_R)
Ag ⁺	449 ^{15,24,35,44-65}	2.11	2.7 ⁹⁴⁻⁹⁶	44.92	0.78
Li ⁺	604 ^{15-30,47,51,66,67}	4.41	4.7 ⁹⁷⁻⁹⁹	49.00	0.94
Cs ⁺	490 ^{15,23,24,31,39}	2.87	6 ³¹	32.31	0.48
Na ⁺	560 ^{15-24,30-37}	3.89	5 ¹⁰⁰⁻¹⁰³	41.49	0.78
H ⁺	264 ^{19,42}	-4.14	1 ⁶	98.04	-4.14
K ⁺	511 ^{15,22-24,36}	3.21	6.4 ^{103,104}	35.35	0.50
Rb ⁺	516 ^{15,23,24,29}	3.28	5 ⁹⁷	34.84	0.66
Cu ²⁺	707 ⁶⁸⁻⁷¹	8.99	6 ¹⁰⁵	94.25	1.50
Sn ²⁺	523 ⁷²⁻⁷⁴	5.46	4.5 ^{72,106}	84.02	1.21
Pb ²⁺	601 ^{22,72,75}	7.22	5.9 ¹⁰⁷⁻¹¹⁰	79.45	1.22
Zn ²⁺	724 ^{19,22,72,78,80-84}	9.22	4.1 ^{103,109-114}	99.61	2.25
Ca ²⁺	798 ^{19,22,23,83,85-89}	10.13	6.6 ^{102,103,109,115-117}	81.91	1.54
Sr ²⁺	765 ^{19,22,23,83,90}	9.75	7.2 ^{103,109,118}	76.56	1.35
Ba ²⁺	749 ^{19,22,23,30,81-83,85,91}	9.55	8.5 ^{85,103,109,115}	70.19	1.12
Fe ²⁺	752 ⁹²	9.59	5.2 ^{92,119,120}	94.71	1.84
Mn ²⁺	742 ⁹⁰	9.46	6 ⁹⁰	96.67	1.58
Mg ²⁺	820 ^{70,83,88,91}	10.37	4.7 ^{109,110,115,116,121,134}	101.45	2.21
La ³⁺	893 ^{41,93}	15.60	6.8 ^{38,103,122,123,125}	119.86	2.29
Sm ³⁺	908 ⁴⁰	15.79	6.9 ^{38,123-125}	124.12	2.29
Tb ³⁺	923 ⁴⁰	15.97	6.1 ^{38,126,127}	128.82	2.62
Ho ³⁺	990 ^{40,41}	16.72	5.8 ³⁸	131.44	2.88
Er ³⁺	1000 ^{40,41}	16.82	6.2 ^{38,123,125,128,130}	131.44	2.71
Yb ³⁺	1018 ^{40,41}	17.00	6.2 ¹²⁵	132.62	2.74
Ce ³⁺	893 ⁴¹	15.60	5.9 ^{38,126,129}	132.05	2.64
Pr ³⁺	913 ⁴¹	15.85	6.6 ^{38,125}	122.32	2.40
Nd ³⁺	903 ⁴¹	15.73	6.6 ^{38,126,128,130}	123.59	2.38

^aValues averaged from results found in the literature.^bCalculated with the ionic radius correspondent to the closest coordination on Shannon and Prewitt's table.¹³¹^cSee text for clarification.

III. CONCLUSIONS

In summary, we considered the treatment of modifier ions in the scope of the temperature-dependent bond constraint theory, using the example of metaphosphate glasses with a broad range of modifier cation species. We found that the theory fails to predict the glass properties because the local environment around the modifiers is not the only parameter which affects their contribution to the rigidity of the glass network. We therefore introduce the concept of constraint strength, which is a simplistic measure of how strongly the modifiers are bound to the surrounding oxygens through long-ranging coulombic forces. This parameter formally integrates all modifier interactions, which presently does not allow to differentiate between short, medium, or long range contributions. While the coulombic forces do seem to influence the strength of the bonding between the modifiers and the non-bridging oxygens, it is not unreasonable to think that they might also act in the medium and long range, effecting the distribution of the modifiers in the glass matrix, for example.

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2.1.2. Modifier Constraints in Alkali Ultraphosphate Glasses

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In applying the recently introduced concept of cationic constraint strength [J. Chem. Phys. 140, 214501 (2014)] to bond constraint theory (BCT) of binary phosphate glasses in the ultraphosphate region of $xR_2O-(1-x)P_2O_5$ (with $x \leq 0.5$ and $R = \{Li, Na, Cs\}$), we demonstrate that a fundamental limitation of the BCT can be overcome. The modifiers are considered to exist in either "isolated" or "crosslinking" sites, in line with the so-called modifier sub-network [J. Chem. Phys. 140, 154501 (2014)] and each site is associated with a certain number of constraints. We estimate the compositional dependence of the modifier sites and then use this to calculate the glass transition temperature as a function of chemical composition. A statistical distribution of sites achieves a remarkable agreement with experimental data for all tested glasses and greatly improves upon previously published work.

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Letter to the Editor

Modifier constraints in alkali ultraphosphate glasses

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ABSTRACT

In applying the recently introduced concept of cationic constraint strength [J. Chem. Phys. 140, 214501 (2014)] to bond constraint theory (BCT) of binary phosphate glasses in the ultraphosphate region of $xR_2O-(1-x)P_2O_5$ (with $x \leq 0.5$ and $R = \{Li, Na, Cs\}$), we demonstrate that a fundamental limitation of BCT can be overcome. The modifiers are considered to exist in either “isolated” or “crosslinking” sites, in line with the so-called modifier sub-network [J. Chem. Phys. 140, 154501 (2014)] and each site is associated with a certain number of constraints. We estimate the compositional dependence of the modifier sites and then use this to calculate the glass transition temperature as a function of chemical composition. A statistical distribution of sites achieves a remarkable agreement with experimental data for all tested glasses and greatly improves upon previously published work.

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1. Introduction

Since the introduction of the concept of temperature-dependent bond constraints [1–4], the bond constraint theory (BCT) has been at the core of several studies with the goal of predicting glass transition temperature, liquid fragility, and surface hardness of various glass systems [5–18]. However, some fundamental limitations of BCT have also been revealed where experimental data can, inherently, not be reproduced by the simple consideration of a “stick-and-ball” model with only short-range interactions between connected and disconnected nodes of a glassy network. For example, classical BCT is unable to distinguish the effects of varying network modifier species with the same coordination number, since they are considered as having identical local topologies. Recent efforts have therefore been dedicated to creating a better understanding of the notion of *bond constraints* in a glass for providing tools to make the theory applicable to a broader range of glass compositions *while maintaining its simplicity*. In this report we aim to consolidate the ideas of the modifier sub-network [5] and the constraint strength parameter [6] into a single framework. We show that in this way, prediction of the glass transition temperature of binary alkali phosphate glasses and, in particular, the effect of varying modifier species is significantly improved.

2. Calculations

In the present study, we employ literature data for the glass transition temperature T_g of Li [19–38], Na [19–30,39–44] and Cs [19–22,45] binary phosphate glasses in the ultraphosphate region (between vitreous phosphorus oxide and the alkali metaphosphate, $xR_2O-(1-x)P_2O_5$ with $x \leq 0.5$ and $R = \{Li, Na, Cs\}$). These binary phosphate glasses are interesting because the phosphorus speciation closely follows Hoppe’s structural model [46], allowing for a clear estimation of the number of phosphate network constraints n_{net} . As recently introduced [6,7], the theoretical value of n_{net} can be compared to a value of n_{sys} which is the number of constraints which the glass should exhibit if it would fully comply with classical BCT according to its experimental T_g . The difference between n_{net} and n_{sys} is the number of “excess” constraints, n_{ex} [1,6],

$$n_{ex}(x, T_g) = n_{sys}(T_g) - n_{net}(x) \quad (1)$$

where x is the compositional variable in the $xR_2O-(1-x)P_2O_5$ glasses and $n_{sys}(T_g)$ is computed through [7]:

$$n_{sys}(T_g) = 3 - \left[\frac{(3 - n^{ref}) T_g^{ref}}{T_g} \right] \quad (2)$$

with the reference composition being pure vitreous phosphorus oxide, therefore $n^{ref} = 3/2$ and $T_g^{ref} = 590$ K [9]. The number of excess

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constraints can be related to the contributions of the modifiers to the network,

$$n_{ex}(x) = K_R \cdot X_R(x) \quad (3)$$

where K_R is the number of constraints per modifier and X_R is the molar fraction of the modifier R. However, according to Hermansen's approach [5] (which is based on Hoppe's structural model) in ultraphosphate glasses the modifier exists in one of two different sites: an "isolated" site, where the modifier is connected to the non-bridging oxygens of one Q^2 phosphorus tetrahedron and several double-bonded oxygens of other phosphate Q^3 tetrahedra if the compositional variable is smaller than some critical composition x_c (defined as $x_c = v/CN_R$ [46], where CN_R is coordination number of the modifier R and v its ionic charge); or a "crosslinking" site, where the modifier effectively acts as a crosslinking agent between two or more distinct Q^2 tetrahedra if $x > x_c$. Both of these sites might add a different number of rigid constraints to the overall glass system, so Eq. (3) can be rewritten as:

$$n_{ex}(x) = [K^{iso} \cdot f_{iso}(x) + K^{cross} \cdot f_{cross}(x)] \cdot X_R(x) \quad (4)$$

where K^{iso} and K^{cross} are the number of constraints per modifier in the isolated and crosslinking sites, and f_{iso} and f_{cross} are the relative fractions of modifier R in each site. Therefore in order to calculate the number of constraints associated with the modifier ions one has to estimate the evolution of the two sites as a function of glass composition and the number of constraints each site adds to the network. Fortunately, at the metaphosphate composition ($x = 0.5$) every phosphorus tetrahedra is a Q^2 species [25,34,47–50], meaning that there are no isolated sites in the glass and that K^{cross} can be easily calculated from the glass transition temperature of the metaphosphate glass. The values of number of constraints per modifier presented by Rodrigues and Wondraczek [6] actually refer to the number of rigid constraints in the crosslinking sites, since the calculations are based only on the glass transition temperatures of the metaphosphate glasses and the equations presented are equivalent to Eq. (4) with $f_{iso}(x) = 0$. Therefore if K^{cross} is known and $f_{cross}(x) = 1 - f_{iso}(x)$, then Eq. (4) can be rewritten as:

$$\left[\frac{n_{ex}(x)}{X_R(x)} - K^{cross} \right] = (K^{iso} - K^{cross}) \cdot f_{iso}(x). \quad (5)$$

Therefore knowledge of the balance between the isolated and the crosslinking sites allows for the estimation of K^{iso} and, finally, of the glass transition temperature as a function of chemical composition. It has been shown that in binary alkali phosphates the distribution of Q^2 and Q^3 species obeys a random distribution [51,52]. If the distribution of the Q^3 species is random, one can calculate the probability of finding the nQ^3 and mQ^2 groups around the modifier ion with a coordination number CN_R via a simple binomial distribution:

$$p(nQ^3, mQ^2) = \binom{n}{n+m} (f_{Q^3})^n (f_{Q^2})^m \quad (6)$$

with $n + m = CN_R$, $0 \leq (n, m) \leq CN_R$ and $f_{Q^3} = (1 - 2x) / (1 - x)$ and $f_{Q^2} = x / (1 - x)$ are the relative fractions of Q^3 and Q^2 species, respectively. However, this distribution implicitly includes the probability of finding a modifier ion surrounded only by Q^3 groups ($n = CN_R$, $m = 0$), which is impossible since there must always be at least one Q^2 connected to the modifier ($m > 0$) in order to maintain charge balance; so the probabilities must be normalized with the only possible distributions ($0 \leq n > CN_R$):

$$p(nQ^3, mQ^2) = \frac{\binom{n}{n+m} (f_{Q^3})^n (f_{Q^2})^m}{\sum_{n=0}^{CN_R-1} \binom{n}{n+m} (f_{Q^3})^n (f_{Q^2})^m}. \quad (7)$$

The fraction of isolated sites can then be estimated with three different approaches: a "step" approximation, assuming that at $x = x_c$, all isolated sites are converted to crosslinking sites (Eq. (8)); a linear approximation, with $f_{iso}(0) = 1$ and $f_{iso}(0.5) = 0$ being the boundaries (Eq. (9)); and a normalized probability approach, with the isolated site having $n = CN_R - 1$ and $m = 1$ (Eq. (10)).

$$f_{iso}^{step}(x) = \begin{cases} 1 & \text{if } x \leq x_c \\ 0 & \text{if } x > x_c \end{cases} \quad (8)$$

$$f_{iso}^{linear}(x) = 1 - 2x \quad (9)$$

$$f_{iso}^{prob}(x) = \frac{\binom{CN_R-1}{CN_R} (f_{Q^3}(x))^{CN_R-1} (f_{Q^2}(x))}{\sum_{n=0}^{CN_R-1} \binom{n}{n+m} (f_{Q^3}(x))^n (f_{Q^2}(x))^m} \quad (10)$$

The coordination numbers and K^{cross} for Li, Na and Cs are summarized in Table 1. In order to simplify the calculations, the coordination numbers were rounded to the closest integer when necessary.

3. Discussion

In Fig. 1 the predicted compositional dependence of the glass transition temperature for binary sodium phosphate glasses from Eqs. (8)–(10) is plotted with literature data [19–30,39–44] for comparison. The step approximation (Eq. (8)) gives a very poor fit to the data, which is not surprising since the underlying assumption that there is an instantaneous conversion of all isolated sites to crosslinking sites at $x = x_c$ is quite unrealistic. The linear approximation (Eq. (9)) does not fare much better, predicting a parabolic change in the glass transition temperature as a function of composition with a minimum around $x = 0.29$. One could try to refine this approach by forcing the fraction of isolated sites to decrease only for $x > x_c$, so that Eq. (9) can be rewritten as:

$$f_{iso}^{linear'}(x) = \begin{cases} x & \text{if } x \leq x_c \\ \frac{1}{(x_c - 1/2)} - \frac{1}{2(x_c - 1/2)} & \text{if } x > x_c \end{cases} \quad (11)$$

The inset in Fig. 1 shows the comparison between Eqs. (9) and (11), showing that also the revised equation does not improve the fit to experimental data. Even though the minimum of the parabola has shifted to smaller values of x , it is still quite distant from x_c .

In contrast, Eq. (10) provides a very good prediction of the compositional dependence of the glass transition temperature for this system. It successfully reproduces the detailed trends shown by the experimental data, including the observed minimum of T_g at $x = x_c$ and the somewhat flat maximum approaching the metaphosphate composition. In Fig. 2 we compare our predictions with Fu and Mauro's [9] and literature data for lithium, sodium, and cesium binary phosphates, and the agreement is remarkable.

Of course, one could argue that our predictions work better simply because we fit the value of K^{iso} from experimental data. This is a necessity since we have recently shown that the number of constraints a modifier

Table 1
Coordination numbers and number of constraints per crosslinking site for Li, Na and Cs in $xR_2O \cdot (1-x)P_2O_5$ glasses [6].

R =	CN_R	K^{cross}	K^{iso}
Li ⁺	5	4.41	−0.90
Na ⁺	5	3.89	−4.42
Cs ⁺	6	2.87	−5.07

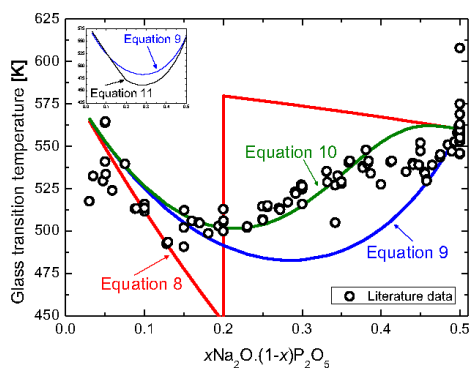


Fig. 1. Glass transition temperature as a function of composition for binary sodium phosphates. The empty symbols are literature experimental data [19–30,39–44] and the solid lines represent the calculated T_g using Eqs. (8), (9), and (10). The inset shows the comparison between the predicted glass transition temperatures between Eqs. (9) and (11).

adds to metaphosphate glasses does not strongly correlate with the modifier's coordination number but is proportional to the strength of the coulombic interactions between the modifiers and the non-bridging oxygens [6]. There are two important consequences to this result: it allows us to explain why the glass transition temperature of the cesium metaphosphate is smaller in comparison with the lithium metaphosphate, even though the coordination number of Cs is larger than the one for Li; but, because we cannot have an *ab initio* estimation of K^{TOS} , we also have no way of determining K^{BP} beforehand.

Even if the overall description of the compositional dependence of the glass transition as a function of composition is enhanced by this model, there are some issues that need to be addressed. Most importantly, there is a definite shift in the maximum of the glass transition temperature from the metaphosphate composition for Li to $x \approx 0.4$ for Cs. It is possible that the increase in the modifier size forces a slightly less random distribution of Q^1 species in its vicinity, resulting in a skewed probability distribution. This might also be the result of using a simple binomial distribution. One of its underlying assumptions is that the probability of finding a Q^1 group around the modifier is independent of how many of this same Q^1 groups are already there and that might be a reasonable approximation when the fraction of Q^3 and Q^2 groups is roughly equal, but in the compositional extremes near the pure phosphate glass and the metaphosphate glass there are very small fractions of Q^1 groups (Q^2 and Q^3 , respectively), perhaps small enough that the presence of this Q^1 group affects the probability of adding another of the same species. In this case the binomial distribution breaks down and one has to use the non-central hypergeometric distribution, which has already been applied to the mixed network former problem by Mauro [53]. Secondly, we find that the best fits result in negative values of K^{BP} for all three modifiers. While this might seem unphysical since there cannot be a negative amount of intact geometric constraints, one has to consider that due to the more ionic character of the chemical bond between the non-bridging oxygen and the modifier the bond lengths and angles become less well defined. We suggest that these negative values are associated with isolated sites due to the molecular rearrangements necessary to accommodate the modifier. This complements our calculations for HPO_3 , which result in -4.14 constraints per hydrogen atom [6], and even though it is a metaphosphate glass the hydrogen atom bonds so strongly to just one non-bridging oxygen that it effectively does not crosslink the network. We would like to highlight the fact that this mathematical approach can only be applied if the coordination number of the modifier is constant as a function of chemical composition. This seems to be a reasonable assumption for the study of binary alkali

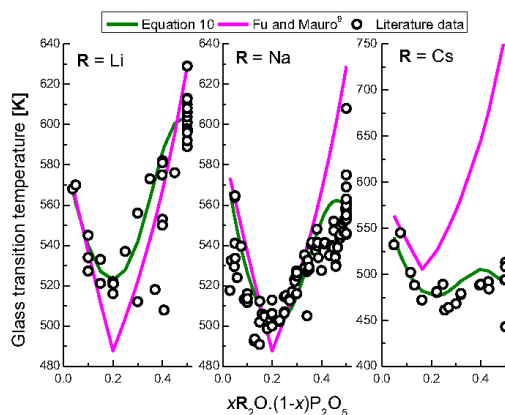


Fig. 2. Glass transition temperature as a function of chemical composition for binary lithium [19–38], sodium [19–30,39–44] and cesium [19–22,45] phosphates. The empty symbols are experimental data from the literature and the lines represent the predicted T_g calculated using Eq. (10) and Fu and Mauro's [9] approach.

phosphates, but further extending this model to describe the dependence of the glass transition temperature of binary phosphate glasses with di- and trivalent modifiers should take the observed change in the coordination number [46,54–56] into account.

4. Conclusions

Combining the concepts of the rigid modifier sub-network and cationic constraints, a new model is developed to calculate the composition dependence of glass transition temperature in ultraphosphates. We consider that the modifiers are present in either isolated or crosslinking sites, each associated with a certain number of constraints per site. The fraction of sites can be calculated via a binomial distribution. The model yields a remarkable agreement with literature data for lithium, sodium, and cesium phosphate glasses, improving upon previously published work.

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2.2. Medium Range Constraints

As discussed previously, the Bond Constraint Theory finds most of its successes in modeling systems where the short-range constraints are the controlling the glass transition temperature, as is the case for $\text{Ge}_x\text{Se}_{1-x}$ ⁴⁸, alkali borates⁸⁵ and metaphosphate glasses⁷⁴. However, the extension of the bond constraint analysis to binary phosphates results in negative values of number of constraints for modifiers in isolated sites⁷⁶. Such outcome is arguably linked to the modifiers affecting other constraints that are not taken into consideration in the calculations, and they could be related to the medium range order (MRO - in the scale of approximately 15 \AA ¹³⁰) of such systems. The presence of MRO in inorganic glasses is usually linked to the First Sharp Diffraction Peak (FSDP) seen in X-ray and neutron diffraction experiments, to the boson peak from Raman scattering and some mechanical properties such as the Poissons ratio and the strain rate sensitivity¹³⁰⁻¹³⁹. Such features are usually related with the localized diffusional movement of the β relaxation¹⁴⁰⁻¹⁴², such as the crankshaft motion and local chain rearrangement in linear polymers¹⁴³⁻¹⁴⁵, and are features widely reported for phosphate glasses^{105, 110, 146-148}.

One manner of investigating such MRO effects is by expanding the Bond Constraint analysis to ternary alkali ultraphosphate glasses, which like many other oxide glasses containing more than one alkali ion in its chemical composition exhibit the so-called Mixed Alkali Effect (MAE). It is characterized by the non-linearity presented by glass properties such as ionic conductivity, glass transition temperature, internal friction and volumetric relaxation with the mixture of alkali species^{149, 150}. One of the most successful models explaining the origin of the MAE is the Dynamic Structure Model (DSM)^{150, 151}, which links the usually observed depression on the glass transition temperature on the “mismatch effect”^{149, 150, 152-163} originating from diverse energy barriers for the diffusion of the modifiers alkali species of different radii are present in the glass and the relaxation the phosphate network undergoes to dissipate the induced stresses caused by the diffusion of ions to sites of dissimilar size. In our work¹⁶⁴ we observed that the MAE can be modeled with the addition of a singular interaction parameter γ to the previously utilized Bond Constraint equations^{74, 76}. This parameter effectively alter the strength of the modifier constraints depending on whether the ions surrounding any given modifier site are occupied by the same chemical species or not. For the systems we analyzed, based on mixed Li^+ alkali glasses, the site distribution of the modifiers was estimated via a simple binomial distribution since NMR data shows that there are no clustering effects¹⁶⁵ and expanding this approach to other glasses is straightforward if this distribution is either known or can be mathematically modeled. It is interesting to note that plotting the parameter γ as a function of the difference in ionic radii of the modifiers present in the glass does not result in a monotonic increase or decrease in its value, instead it displays a minimum. For the mixed Li^+ alkali glasses this minimum is found between a size difference from 20 to 40 pm. It is suggested that such behaviour comes from the interplay of two effects: first, as the size difference increases the distortion caused by the diffusion of modifiers to dissimilar sites, forcing the phosphate

network to rearrange itself to decrease the induced stresses, ultimately weakening the number of constraints and diminishing the value of γ ; secondly, the increase in the size difference also reduces the probability of successful jumps to dissimilar sites, decreasing the overall diffusivity and increasing the effective value of the interaction parameter. One could also expand this interpretation to the calculated negative values for the number of constraints associated with isolated modifier sites in ultraphosphate glasses^{76, 166}: increasing the modifier concentration depolymerizes the phosphate network from a 3D interconnected network to linear chains. Since the linear parts of the network are less constrained due to the bonds to modifiers substituting bonds to other phosphate tetrahedra, they exhibit more degrees of freedom, and therefore require less energy to rearrange themselves, which in turn leads to a larger than expected depression of the glass transition temperature. In this case the number of constraints associated with isolated sites do not represent the actual number of constraints, after all the isolated sites are not part of the network and therefore should not influence the overall number of constraints. Instead, they would represent the additional degrees of freedom gained by the phosphate network as it becomes more and more depolymerized¹⁶⁷, similarly to the observed decrease on the glass transition temperature of thermoset resins as the crosslinking density decreases¹⁶⁸⁻¹⁷⁰.

Another interesting system to which to analyze the effect of the medium range order is the silver metaphosphate – silver halide system. NMR data has shown that the addition of silver iodide to silver phosphates does not affect the speciation of the phosphorus tetrahedra¹⁷¹⁻¹⁷³, meaning that the halides are incorporated in the interstices between the phosphate chains and lead to an increase in interchain spacing. Such glass systems, especially AgPO₃-AgI, have been widely studied due to their relatively high ionic conductivity at room temperature, which is attributed to the increase on effective charge carriers with increasing silver iodide content¹⁷⁴. The distribution and structure of the incorporated silver iodide has been the focus of several studies, with experimental data being interpreted either as the presence of α -AgI clusters¹⁷⁵⁻¹⁷⁸ or as an amorphous interstitial phase^{171, 172, 179, 180}; the more recent studies favour the amorphous phase hypothesis. Therefore this system provides the rather rare opportunity of studying the effect of the halide addition without changing the short range environment of the phosphate groups. With ample literature data on the glass transition temperature dependence on halide concentration for silver metaphosphate – silver halide glasses¹⁶⁶, we showed that the halide bearing glasses are, according to the Temperature Dependent Bond Constraint Theory, overconstrained when compared with the expected number of constraints from the substitution of the phosphate groups by the halides. The silver-halide constraints are not counted since they are supposed to be completely broken at temperatures lower than the glass transition, and this conjecture is strengthened by the fact that the glass transition temperature dependence of halide concentration is effectively independent with the addition of silver chloride, silver bromide or silver iodide. This excess constraints were explained in terms of the conversion of the metaphosphate chains to rings as the halide concentration increases, as reported by Novita *et al.*¹⁸¹. It is well known from polymer studies that beyond a threshold polymerization degree,

as it decreases the glass transition temperature of linear chains decreases while the glass transition temperature of rings increase¹⁸², a fact which is still not very well understood but might be due to their smaller radius of gyration¹⁸³. A recent thorough study by Palles *et al.*¹⁸⁴ on silver metaphosphate - silver iodide glasses reinforces the already established view that the addition of the halide leaves the phosphate groups largely untouched, but suggest that the previously observed chain to ring conversion is actually an effect of the leaching of alumina into the glasses, which leads to the formation of crosslinking sites between phosphate chains. They also suggest that there is a small but systematic change on the Raman and FITR spectra of such glasses imply that there are phosphate rings being opened and the overall chain size being shortened. One must note that they also report the glass transition temperature of their glasses, which are very much in line with the literature values covered in our paper¹⁶⁶, so even if the origin of the excess constraints is not on the chain to ring ratio, it might still be due to intermediate range effects, such as the iodine ions steric hindering the movement of the phosphate chains, since these glasses also show an smaller free volume when compared with the metaphosphates¹⁷⁴.

2.2.1. Modifier Interaction And Mixed-Alkali Effect In Bond Constraint Theory Applied To Ternary Alkali Metaphosphate Glasses

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Introducing an interaction parameter γ , we implement modifier interaction and the mixed-alkali effect into bond constraint theory, and apply this extension for simplistic property prediction on ternary phosphate glasses. The severity of the mixed alkali effect results from the interplay of two simultaneous contributions: Bond constraints on the modifier species soften or stiffen with decreasing or increasing γ , respectively. When the modifier size is not too dissimilar the decrease in γ reflects that the alkali ions can easily migrate between different sites, forcing the network to continuously re-accommodate for any subsequent distortions. With increasing size difference, migration becomes increasingly difficult without considerable network deformation. This holds even for smaller ions, where the sluggish dynamics of the larger constituent result in blocking of the fast ion movement, leading to the subsequent increase in γ . Beyond a certain size difference in the modifier pair, a value of γ exceeding unity may indicate the presence of steric hindrance due to the large surrounding modifiers impeding the phosphate network to re-accommodate deformation.

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Modifier Interaction and Mixed-Alkali Effect in Bond Constraint Theory Applied to Ternary Alkali Metaphosphate Glasses

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Keywords: mixed-alkali effect, glass transition temperature, bond constraint theory, phosphate glasses, topological constraints

INTRODUCTION

The bond constraint theory (BCT), as originally formulated by Phillips (1979) and Phillips and Thorpe (1985), rationalizes the glass structure in terms of a simple “ball-and-stick” network. It uses topological relationships based on the number of linear and angular constraints found on the first coordination shell of each atom within the glass network. More recently, Gupta and Mauro (2009) and Mauro et al. (2009) introduced the concept of temperature-dependent constraints, based on previous work by Naumis (2005, 2006), taking into account the temperature dependence of configurational entropy and, hence, the number of bond constraints. This allowed for applying constraint counting to calculate the compositional trends of properties, such as the glass transition temperature (Gupta and Mauro, 2009; Mauro et al., 2009; Smedskjaer et al., 2010b, 2011; Fu and Mauro, 2013; Jiang et al., 2013; Rodrigues and Wondraczek, 2013, 2014; Hermansen et al., 2014a; Rodrigues et al., 2014), fragility (Gupta and Mauro, 2009; Mauro et al., 2009; Hermansen et al., 2014a), and surface hardness (Smedskjaer et al., 2010a,c, 2011; Wondraczek et al., 2011; Smedskjaer, 2014). While useful applications of the BCT need detailed structural information, the strength of this approach lies in its simplicity, as only the knowledge of the components’ first shell coordination number and a

reasonable guess about the relative strength of the constraints considered are required for relatively accurate property prediction. However, the BCT is not without problems, which start already with its basic assumptions (Rodrigues and Wondraczek, 2015) as how to incorporate structural influences beyond the short range (Rodrigues and Wondraczek, 2013). In glass science, one such example is the so-called “mixed-alkali effect” (MAE), where the mixture of two alkali species results in a non-linear variation of several properties, such as ionic conductivity, glass transition temperature, internal friction, and volumetric relaxation (Bunde et al., 2004; Changstrom and Sidebottom, 2008). Here, we, therefore, aim to expand the current understanding of the BCT toward incorporation of such non-linear interaction terms, choosing the example of mixed-alkali phosphate glasses (Fu and Mauro, 2013; Hermansen et al., 2014a; Rodrigues and Wondraczek, 2014; Rodrigues et al., 2014). We demonstrate how appropriate interaction terms can be used to incorporate the MAE into BCT so as to enable accurate calculation of the glass transition temperature. However, we also show that in doing so, the empiricism of the approach is further highlighted, because the physical meaning of the required fitting parameters is presently not developed.

MODIFIER CONSTRAINTS

The BCT was originally developed and applied to chalcogenide glasses, which are particularly suitable to the “ball-and-stick” analogy, since the atoms are connected by predominantly covalent bonds with very well-defined first coordination shells, similar to the bonds between oxygen and the network formers in most oxide glasses. It was previously assumed that the number of constraints associated with each modifier atom within the glass network depends exclusively on its first coordination shell (Fu and Mauro, 2013). However, we have later shown that while the coordination number influences the number of constraints, the actual interaction strength is mainly a function of the electrostatic forces between the modifier and the non-bridging oxygens (Rodrigues and Wondraczek, 2014), in accordance with the observations of Eisenberg et al. (1966) several decades ago. The interactions between the non-bridging oxygens and the network modifiers have a strongly ionic character. This requires adaptations to the “ball-and-stick” model due to the lower directionality and longer ranges characteristic of the Coulombic interactions. This adaptation was achieved by the introduction of the characteristic “constraint strengths” to the model, for which there are now two ways of implementation: in our previous work (Rodrigues and Wondraczek, 2014; Rodrigues et al., 2014), we argue that the “constraint strength” defined as the ratio between the number of constraints each modifier R adds to the system (K_R) and its coordination number (CN_R) represents the number of constraints each modifier/non-bridging oxygen bond adds to the system, with the caveat that the numbers are relative to the absolute strength of all other constraints which are assumed to be equal to unity. Alternatively, Hermansen et al. (2014b) argue that the “constraint strength” (q_T in this notation) also represents the fraction of the modifier constraints that are still intact at the

temperature in question. Both approaches result in equivalent glass transition temperature predictions for the studied binary phosphate glasses and both “constraint strength” values are linearly dependent on the Coulombic forces between the modifiers and non-bridging oxygens (Hermansen et al., 2014b; Rodrigues and Wondraczek, 2014). In this work, we will be using the former interpretation for two main reasons: first, it provides internal consistency on how the modifier constraints are treated, being considered either completely broken or completely intact, the same as all other constraints present in the system. Second, and more importantly, the distribution of modifier sites according to the calculations from Hermansen et al. (2014b) does not seem to correspond to experimental data. According to Hermansen et al. (2014b), the number of modifier constraints is given by $2 \times X_R(x)$ for $x \leq x_{crit}$ and $CN_R \times X_R(x - x_{crit}) + 2 \times X_R(x_{crit})$ for $x > x_{crit}$, where $X_R(x)$ is the modifier’s molar fraction, x is the compositional variable as in $xR_2O \times (1 - x)P_2O_5$ and x_{crit} is Hoppe’s critical composition ($x_{crit} = v/CN_R$, with the modifier valency v) (Hoppe, 1996), above which the number of double-bonded oxygens is not enough to fully coordinate the modifier ions, which in consequence begin to share non-bridging oxygens and effectively repolymerize the phosphate network. One can see that according to these equations, even at the metaphosphate composition ($x = 0.5$), there would still be a finite number of modifiers that should be surrounded by double-bonded oxygens since $2 \times R(x_{crit}) > 0$, but from ^{31}P NMR measurements, it is known that at the metaphosphate composition there are no (or almost no) Q^3 groups and, therefore, double-bonded oxygens (Brow, 2000) and also NMR from the modifiers does not show evidence for more than one site (Schneider et al., 2013). On the other hand, for this study, the values of constraints per modifier (K_R) as they are listed in Rodrigues and Wondraczek (2014) were recalculated, as the previous calculation used an inconsistent counting of the phosphate network constraints (Hermansen et al., 2014a). The final values of K_R are shown in Table 1.

BOND CONSTRAINT MODELING OF THE MIXED-ALKALI METAPHOSPHATES

Continuous investigation on the nature of the MAE over the last 30 years has uncovered convincing evidence that the structural basis for this effect lies in the “mismatch effect” (Angell, 1990, 1992; Huang and Cormack, 1992; Hunt, 1997; Maass, 1999;

TABLE 1 | Number of constraints per modifier, K_R , for alkali and silver metaphosphate glasses.

Modifier	K_R	Coordination number ^a
Li ⁺	3.07	5
Na ⁺	2.84	5
K ⁺	2.53	6
Rb ⁺	2.55	5
Cs ⁺	2.37	6
Ag ⁺	2.03	3

^aData from Rodrigues and Wondraczek (2014) rounded to the closest integer.

Adams and Swenson, 2002; Fang et al., 2003; Bunde et al., 2004; Hall et al., 2004; Ingram et al., 2006; Puls and Eckert, 2006; Changstrom and Sidebottom, 2008; Dieterich and Maass, 2009; Dyrre et al., 2009), as described by the dynamic structure model (DSM) of Bunde et al. (2004) and Ingram and Roling (2003). A simplified description of the model goes as follows: in a single alkali glass, the modifiers A reside in sites that match their requirements for coordination number and distance between the modifier and the non-bridging oxygens. The diffusion of such ions does not require large rearrangements from the glassy network, since all modifier sites are similar. However, the addition of a second modifier B to this same glass results in the presence of two different types of modifier sites, and while it remains possible for the modifiers to jump from similar to similar sites, there is also the possibility of jumps between dissimilar sites, especially as the ratio of A/B cations approaches unity. Ingram and Roling (2003) argue that the motion of cations to dissimilar sites causes the network to reconfigure itself so as to minimize the distortions caused by the presence of an A atom on a B site (or a B atom on a A site). If the cations are statistically distributed on the glass structure, one would expect that at the molar ratio of A/B of unity, the probability of the modifiers to jump to dissimilar sites is maximized, leading to an increased flexibility of the glassy network and the often observed depression of the glass transition temperature at compositions close or at A/B = 1.

From the mentioned concepts, we can assume that the number of constraints a modifier A adds to the glass network depends not only on its first coordination shell, comprised solely by non-bridging oxygens in the case of the phosphate glasses we are focusing on, but also on the neighboring sites the modifier can access. Therefore, the number of constraints depends not only on how strongly the modifiers are bonded to the non-bridging oxygens but also on how often they jump to surrounding modifier sites. This does not affect the calculated values shown in Table 1, because for binary metaphosphate glasses the number of constraints already takes into account the movement of the modifier to sites previously occupied by the same modifier (modifier A jumping from an A site to another A site).

Considering a mixed-alkali metaphosphate glass of composition $yA_2O \times (0.5 - y)B_2O \times 0.5P_2O_5$, the number of constraints that the modifiers add to the network (n_M) can be written as:

$$n_M(y) = n_A(y) + n_B(y) \quad (1)$$

where n_A and n_B are the number of constraints the cations A and B add to the network.

According to Rodrigues and Wondraczek (2014) and Rodrigues et al. (2014), n_A and n_B are a function of the number of constraints per modifier (K_R) and their molar fraction (X_R). The weakening of the modifier constraints due to the presence of cations in dissimilar sites is modeled with the addition of the term T_R . One must note that this should only apply to the sites the modifier in question can effectively access, or, in other words, the term T_R should only modify the number of constraints of cross-linking sites; therefore, the use of mixed-metaphosphate glasses simplifies the calculations, since, at this composition, all modifier sites are cross-linking or, alternatively, no modifier

exists in isolated sites (Rodrigues et al., 2014), so Eq. 1 can be written as:

$$n_M(y) = K_A \times X_A(y) \times T_A(y) + K_B \times X_B(y) \times T_B(y) \quad (2)$$

where T_A is defined as:

$$T_A(y) = \sum_{i=0}^{CN_A} G_{CN_A-i,i} \times p_{CN_A-i,i}(y) \quad (3)$$

CN_A is the modifier's coordination number (or closest integer), $p_{CN_A-i,i}$ is the probability of finding an A site with CN_{A-i} A atoms and i B atoms surrounding it and $G_{CN_A-i,i}$ is defined as:

$$G_{CN_A-i,i} = \frac{[(CN_A - i) \times \gamma_{AA}] + [i \times \gamma_{AB}]}{CN_A} \quad (4)$$

Here, γ_{AA} and γ_{AB} are factors that illustrate how the constraints are changed as the modifiers migrate to neighboring sites that are either the same as the original one, or different from the original one. γ_{AA} is fixed at unity, because there is no change to the constraint strength as the modifiers move to similar sites, as argued previously. If the modifiers are homogeneously distributed throughout the glassy network, then the probabilities of finding the different sites $p_{CN_A-i,i}$ can be calculated *via* a simple binomial distribution (Eq. 5), akin connections between Q^2 and Q^3 groups (Alam and Brow, 1998; Alam et al., 2000).

$$p_{CN_A-i,i}(y) = \binom{CN_A - i}{CN_A} \times \left(\frac{X_A(y)}{X_A(y) + X_B(y)} \right)^{CN_A-i} \times \left(\frac{X_B(y)}{X_A(y) + X_B(y)} \right)^i \quad (5)$$

So, the number of constraints the modifier A adds to the network can be written as:

$$\begin{aligned} n_A(y) &= K_A \times X_A \times \left[G_{CN_A,0} \times p_{CN_A,0} + G_{CN_A-1,1} \times p_{CN_A-1,1} \right. \\ &\quad \left. + \dots + G_{0,CN_A} \times p_{0,CN_A} \right] \quad (6) \\ n_A(y) &= K_A \times X_A(y) \times \left[\left(\frac{CN_A \times \gamma_{AA} + 0 \times \gamma_{AB}}{CN_A} \right) \right. \\ &\quad \times p_{CN_A,0} + \left(\frac{CN_A - 1 \times \gamma_{AA} + 1 \times \gamma_{AB}}{CN_A} \right) \\ &\quad \left. \times p_{CN_A-1,1} + \dots + \left(\frac{0 \times \gamma_{AA} + CN_A \times \gamma_{AB}}{CN_A} \right) \times p_{0,CN_A} \right] \quad (7) \end{aligned}$$

As $\gamma_{AA} = 1$:

$$\begin{aligned} n_A(y) &= K_A \times X_A(y) \times \left[p_{CN_A,0} + \left(\frac{CN_A - 1 + \gamma_{AB}}{CN_A} \right) \right. \\ &\quad \times p_{CN_A-1,1} + \dots + \left(\frac{1 + CN_A - 1 \times \gamma_{AB}}{CN_A} \right) \\ &\quad \left. \times p_{1,CN_A-1} + \gamma_{AB} \times p_{0,CN_A} \right] \quad (8) \end{aligned}$$

Rearranging Eq. 8, we get:

$$n_A(y) = K_A \times X_A(y) \times [J_A(y) + \gamma_{AB} \times L_A(y)] \quad (9)$$

with

$$J_A(y) = \sum_{i=0}^{CN_A-1} \left(\frac{CN_A - i}{CN_A} \right) \times p_{CN_A-i}(y) \quad (10)$$

$$L_A(y) = \sum_{i=1}^{CN_A} \left(\frac{i}{CN_A} \right) \times p_{CN_A-i,1}(y) \quad (11)$$

which can be rewritten as:

$$n_A(y) = J_A^*(y) + \gamma_{AB} \times L_A^*(y) \quad (12)$$

If

$$J_A^*(y) = K_A \times X_A(y) \times J_A(y) \quad (13)$$

$$L_A^*(y) = K_A \times X_A(y) \times L_A(y) \quad (14)$$

Substituting Eq. 12 for both **A** and **B** cations in Eq. 1 yields:

$$n_M(y) = J_A^*(y) + \gamma_{AB} \times L_A^*(y) + J_B^*(y) + \gamma_{BA} \times L_B^*(y) \quad (15)$$

Assuming that $\gamma_{AB} = \gamma_{BA} = \gamma$, we have that:

$$n_M(y) = (J_A^*(y) + J_B^*(y)) + \gamma \times (L_A^*(y) + L_B^*(y)) \quad (16)$$

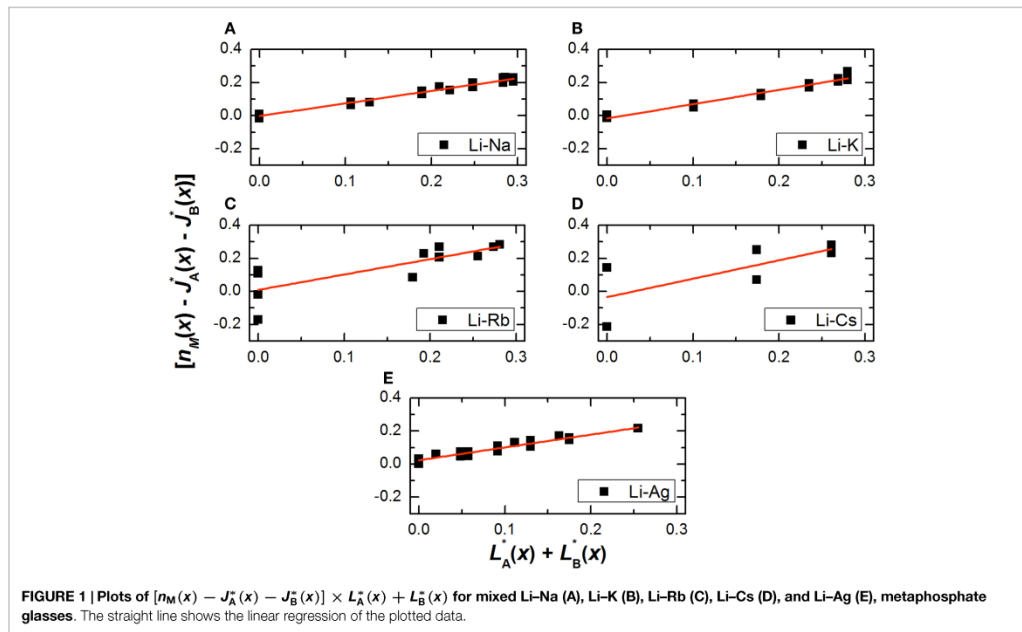
or,

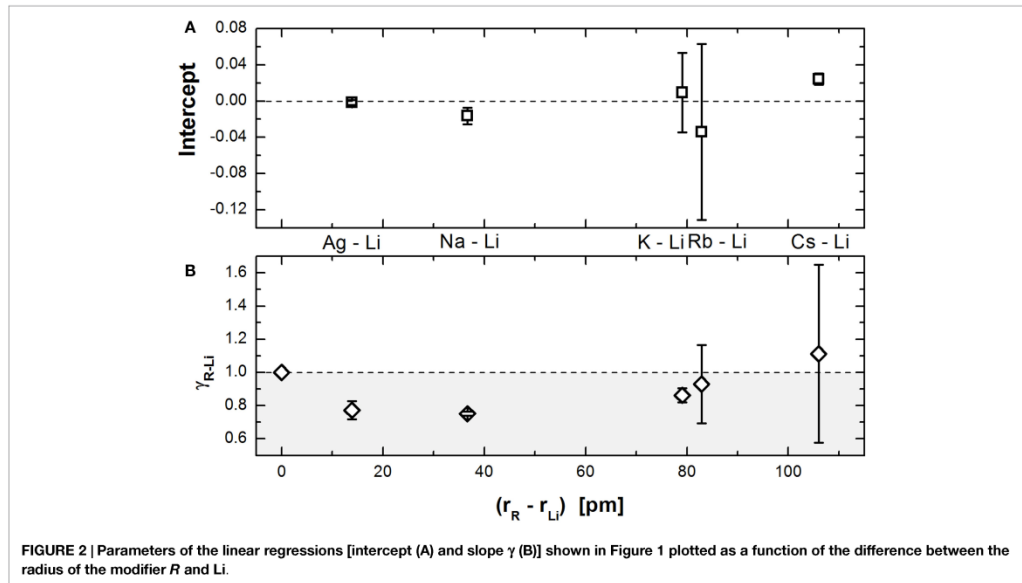
$$[n_M(y) - J_A^*(y) - J_B^*(y)] = \gamma \times (L_A^*(y) + L_B^*(y)) \quad (17)$$

Equation 17 presents an important formulation, because it states that the number of constraints the modifiers add to the glassy network is linearly proportional to J_A^* , J_B^* , L_A^* , and L_B^* , the quantities that can be calculated with knowledge of the glass composition and the coordination number of the modifiers in question. In order to test the applicability of Eq. 17, we took glass transition temperature data for Li–Na, Li–Ag, Li–K, Li–Rb, and Li–Cs metaphosphate glasses from the literature (Eisenberg and Saito, 1966; Denoyelle et al., 1990; Doreau and Robert, 1991; Green et al., 1999; Sidebottom et al., 1999; Bandaranayake et al., 2002; Changstrom and Sidebottom, 2008; Hall et al., 2009; Tsuchida et al., 2012), since it has been shown by NMR measurements that there is no modifier clustering (Schneider et al., 2013), which we assumed in our derivation. Noteworthy, the present approach, therefore, cannot be used for analyzing glasses where the modifier distribution shows a pronounced divergence from random mixture, such as Na–K, Na–Rb, or Na–Cs mixed-metaphosphate glasses (Tsuchida et al., 2012).

RESULTS AND DISCUSSION

Figure 1 shows the plots of $[n_M(y) - J_A^*(y) - J_B^*(y)]$ as a function of $L_A^*(y) + L_B^*(y)$ for the five aforementioned glass systems, whereas **Figure 2** shows the parameters from the linear regression of the data as a function of the difference in atomic





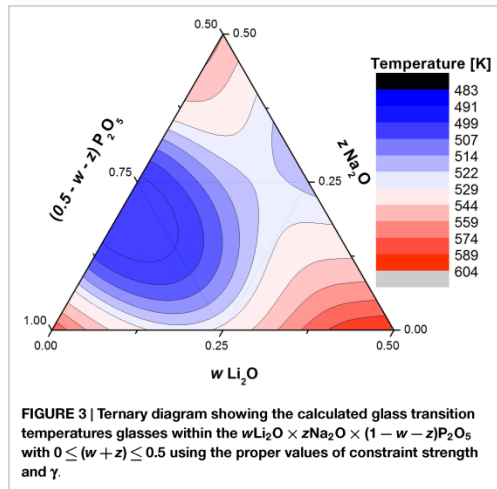
radius between both modifiers. It should be noted that while the expected linear behavior is observed for all glasses, there is some scatter especially on **Figures 1C,D**, mainly because there are fewer datasets available for the Li–Rb and Li–Cs mixed metaphosphates, so that the number of constraints on **Table 1** are not exactly representative.

Figure 2A shows that the intercept is very close to 0, practically independent of the pair of modifiers, while the value of γ (**Figure 2B**) shows an interesting dependence on the modifier size difference. The minimum present at size differences around 40 pm seems to indicate that the severity of the MAE results from the interplay of two simultaneous responses: one that softens the constraints on mixed sites and another that stiffens them (decreasing and increasing γ , respectively). When the modifier size is not too dissimilar, the net decrease in γ reflects that the alkali ions can easily move to different sites, forcing the network to continuously reaccommodate itself for the distortions caused by the presence of the modifiers in different sites. As the size difference increases, it becomes increasingly difficult for the modifiers to reach sites smaller than themselves without considerable network deformation, up to a point where the larger ions are bound to jump only to their own sites as they do not fit inside the others. So, even if the smaller ions can easily move between their own sites and the larger sites, the sluggish dynamics of the larger ions block the movement of the faster ions, decreasing the amount of reaccommodation the network suffers and subsequently increasing γ .

Another very interesting feature on **Figure 2B** is that beyond a certain size difference (roughly between 85 and 115 pm), the value of γ becomes greater than unity. This effectively means that the constraints would be stiffer in mixed sites, in contrast with what is expected from the current theoretical understanding. We suggest

that this effect happens due to the larger ions sterically hindering the phosphate network. This is important because Ingram and Roling (2003) argue that the flexibility of the network, which allows for it to rearrange itself as the ions move in and out of dissimilar sites, is the rationale behind the observed decrease on the constraints.

These results highlight some of the advantages and disadvantages of using the BCT to model the glass transition temperature of oxide glasses. It is definitely advantageous that the theory is flexible enough to be easily modified to account for non-linear effects, such as the repolymerization of the phosphate network and the MAE. It is also simple enough so that almost any result can be adapted and remain self consistent. The analysis developed by Rodrigues et al. (2014) and this present paper can be used in conjunction to model the glass transition of a ternary phosphate system with knowledge of the coordination number of the two modifiers and the glass transition of only four compositions: vitreous phosphorus, both binary metaphosphates, and the $A/B = 1$ mixed metaphosphate (**Figure 3** for the Li–Na metaphosphate system). This is a very quick and effortless way to generate the complete ternary diagram with a minimum of four glass transition temperature measurements. On the other hand, the BCT does not provide the tools to allow for the calculation of the values of constraint strength and γ , so, while they tie in reasonably well with some material properties, in order to use the correct values, one must always resort to use experimental data. Another open question is whether the trend observed in **Figure 2** is valid for all modifier pairs and all other glass-forming oxides (such as silicates, borates, and germanates), or if the values of γ depend on the network, the modifiers are embedded within, much like the values of the constraint strength (Rodrigues and Wondraczek, 2015); or



if they also depend on the pair of modifiers in question, meaning that the data points for mixed Na–R metaphosphate glasses would be shifted from the Li–R and so on.

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CONCLUSION

We showed that the BCT can be extended to model the glass transition temperature of mixed-alkali metaphosphates and that the “mixed-alkali effect” can be parameterized with the addition of a single variable γ , which can be calculated with the knowledge of the coordination numbers of the two modifiers and the glass transition temperatures of the two binary metaphosphate glasses and the $A/B = 1$ composition. The reported results follow the same pattern of other BCT applications, showing good agreement between model and experimental data with few fitting parameters. But BCT does not present a way of estimating the fitting parameters *ab initio*, and their physical meaning is presently not developed.

AUTHOR CONTRIBUTIONS

This manuscript was written through the contributions of all authors.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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2.2.2. Medium-Range Topological Constraints In Binary Phosphate Glasses

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The theory of temperature-dependent topological constraints has been used to successfully explain the compositional dependence of glass properties for oxide and non-oxide compositions. However, even though the predictions are qualitatively accurate, not all quantitative predictions are as precise. Here, we report on the applications of this theoretical framework to available data for binary phosphate and silver metaphosphate - silver halide glasses. We find that some compositions are overconstrained and some are underconstrained relative to the predicted values. We suggest that the origin of this difference is due to the presence of medium-range constraints such as sterical hindrance which is dependent on packing density and chain length.

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Medium-range topological constraints in binary phosphate glasses

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The theory of temperature-dependent topological constraints has been used to successfully explain the compositional dependence of glass properties for oxide and non-oxide compositions. However, even though the predictions are qualitatively accurate, not all quantitative predictions are as precise. Here, we report on the applications of this theoretical framework to available data for binary phosphate and silver metaphosphate – silver halide glasses. We find that some compositions are overconstrained and some are underconstrained relative to the predicted values. We suggest that the origin of this difference is due to the presence of medium-range constraints such as steric hindrance which is dependent on packing density and chain length. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4810868>]

I. INTRODUCTION

“Topological engineering” of glasses has obtained significant attention recently as it appears to provide a knowledge-based tool for the identification of glass compositions with specific properties.¹ Thereby, the term “topology” is used to describe the short- and mid-range structural architecture which is defined by potentials and spatial relations between constituents on the atomistic level. The basis of this concept was laid by Phillips and Thorpe,^{2,3} who demonstrated that by analyzing the topology of the glass network one can gain valuable insight on the relation between the properties of a glass and its chemical composition. According to their approach the changes in the glass topology are related to changes in the relation of the number of atomic degrees of freedom and the number of atomic constraints. If there are more degrees of freedom than constraints, the network is called “floppy.” On the other hand, if the number of constraints is larger than the degrees of freedom the network will percolate and form a rigid structure.³ Treating the glass network as rigid polytopes connected by vertices, Gupta⁴ derived a description which was mathematically equivalent⁵ to the Phillips-Thorpe model. Both these approaches assume that the number of constraints is independent of temperature, meaning that they are formulated for zero temperature conditions. Expanding on these foundations, Gupta and Mauro⁵ considered the effect of the temperature on the number of atomic constraints and proposed a temperature-dependent constraint model. Adding this temperature dependence enables the theory to connect the number of constraints with the viscosity of glass systems through the configurational entropy.^{5–7} Therefore one can relate the glass transition temperature and the configurational entropy at the glass transition temperature between two glasses of similar composition as follows:

$$\begin{aligned} \frac{T_g(x)}{T_g(x_R)} &= \frac{S_c(T_g(x_R), x_R)}{S_c(T_g(x), x)} = \frac{f(T_g(x_R), x_R)}{f(T_g(x), x)} \\ &= \frac{d - n(T_g(x_R), x_R)}{d - n(T_g(x), x)}, \end{aligned} \quad (1)$$

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where $T_g(x)$ is the glass transition temperature for a glass of chemical composition x , $S_c(T_g(x), x)$ is the configurational entropy at T_g , $f(T_g(x), x)$ is the number of atomic degrees of freedom (also referred to as floppy modes), d is the dimensionality of the network, and $n(T_g(x), x)$ is the number of atomic bond constraints.

Then, with a comprehensive knowledge of the glass structure one can simply count the number of bond constraints per atom and estimate the dependence of the glass transition temperature on chemical composition. This approach has been applied successfully for $\text{Ge}_x\text{Se}_{1-x}$,⁸ binary alkali borates,⁶ sodium borosilicates,⁸ sodium calcium borates,⁹ and, most recently, binary alkali phosphates.¹⁰

One of the most interesting characteristics of phosphate glasses is that they show a minimum of the glass transition temperature,^{11,12} packing density,^{13–15} and ionic volume fraction^{13,16} as the composition changes. Trying to explain these reported anomalies in alkaline earth and zinc ultraphosphate glasses ($2.5 \leq [\text{O}]/[\text{P}] < 3$), Hoppe developed a structural model¹⁷ which described not only the changes in phosphate speciation but also the coordination environment of the modifiers. The phosphate tetrahedra are classified using the Q^i terminology, with the superscript i representing the number of bridging oxygens per tetrahedron.¹⁸ The model developed by Hoppe predicts that for a binary phosphate glass of composition $x\text{R}_{2/v}\text{O} \cdot (1-x)\text{P}_2\text{O}_5$ (where v is the ionic charge of the modifier), in the ultraphosphate compositional region, there is a critical composition x_{cr} which delimits two different topologies: in Region I the number of non-bridging oxygens is larger than the coordination number of the modifier, what essentially isolates their coordination polyhedra from each other; and in Region II the number of non-bridging oxygens is smaller than the coordination number of the modifier, forcing their coordination polyhedra to share corners or edges to maintain their coordination environment and causing a repolymerization of the glass network. A comprehensive review on the structure of phosphate glasses is given by Brow.¹⁸ The boundary between these two glass topologies occurs when the number of non-bridging oxygens equals the coordination number of the modifier (CN_R), at the composition x_{cr} , which can be

easily calculated as follows:

$$x_{cr} = v \left(\frac{1}{CN_R} \right). \quad (2)$$

Probably the greatest achievement of the topological analysis of Fu and Mauro¹⁰ was the quantitative link which was found between the changes in the glass transition temperature and the repolymerization process taking place in Region II. The approach assumes that the relevant constraints are given by the bond constraints from the network forming phosphate units and, from Region II onwards, the ones from the modifier coordination sphere. Consequently, the observed decline in the glass transition temperatures in Region I results from the substitution of the phosphate tetrahedra by the modifiers and the change from Q^3 to Q^2 units, leading to a depolymerized network. Considering that the number of constraints associated with each Q^n unit is constant and as their concentration can be easily calculated from Hoppe's structural model, we can predict the glass transition temperature as a function of composition. Additionally, in Region I this rate should be the same for every binary glass with modifiers of equivalent charge.

II. NUMBER OF CONSTRAINTS IN BINARY PHOSPHATES WITH MONOVALENT CATIONS

To test the statement of a predictable number of constraints (Eq. (1)), we took published glass transition temperature data for several binary phosphates with monovalent ions: H^+ ,¹⁹ Li^+ ,^{11,20–22} Na^+ ,^{12,20,22–25} K^+ ,²⁶ Cs^+ ,^{22,27} and Ag^+ .^{28–53} The number of atomic constraints $n(x)$ was calculated rewriting Eq. (1) as

$$n(x) = 3 - \left[(3 - n(x_R)) \frac{T_g(x_R)}{T_g(x)} \right]. \quad (3)$$

We take vitreous P_2O_5 as the reference glass, therefore we have $n(x_R) = 3/2$ and $T_g(x_R) = 590$ K¹⁰ and estimated the number of constraints only the phosphate network should have via Eq. (4),

$$n_{network}(x) = (2 \times X_{BO}(x)) + (3 \times X_{Q3}(x)) + (1 \times X_{Q2}(x)), \quad (4)$$

where X_{BO} is the fraction of bridging oxygens, X_{Q3} is the fraction of Q^3 coordinated phosphorus, and X_{Q2} is the fraction of Q^2 coordinated phosphorus.

As one can see from Figure 1, there is reasonable agreement between Eq. (4) and the measured values only until $x \sim 0.1$. For $x > 0.18$, the observed increase in the number of constraints is associated with the transition from Region I to Region II in the structural model of Hoppe,¹⁷ leaving a compositional window of x between 0.1 and 0.18 where deviations from the expected behavior occur in both directions, depending on the cation species, i.e., under- and overestimating $n(x)$.

Figure 1 has some interesting features. Firstly, according to the approach of Fu and Mauro,¹⁰ the metaphosphoric acid HPO_3 should have a negative number of constraints to attain its glass transition temperature of 263 K.⁵⁴ Even so, HPO_3 actually shows good glass forming abilities^{23,24,54} and it is

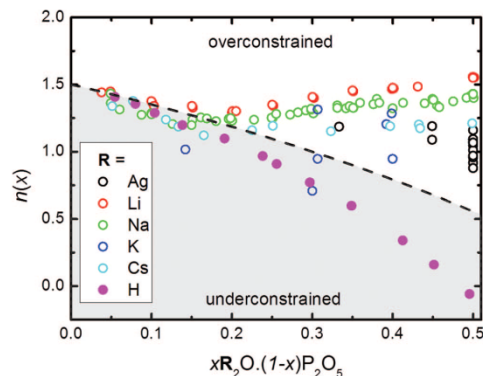


FIG. 1. Number of atomic constraints $n(x)$ as a function of glass composition. The dashed line represents only the constraints of the phosphate network (Eq. (4)), the open symbols are values calculated from experimental data and the closed symbols are from modelling.¹⁹

possible to synthesize phosphoric acids with even greater water content, reaching glass transition temperatures as low as 151 K¹⁹ which would correspond to approximately -2.8 constraints per atom. That is, for this specific case, the system is more constrained in reality than it should be according to the present theory of temperature-dependent constraints.

Another interesting feature is the point of deviation from the predicted values. As previous works on the temperature-dependent constraint theory have already illustrated,^{5,6,8–10} changes in the glass transition temperature can be associated to changes in the glass topology. According to Hoppe's structural model for binary phosphate glasses,¹⁷ there is a change in the network topology at a certain composition, given by Eq. (2), where the modifier atoms start acting as bridges between separate phosphate chains, leading to an increase in the glass transition temperature of these glasses. This transition is governed by the coordination number and ionic charge of the modifier. Fu and Mauro's analysis of the constraints in phosphates assume that, in the compositional Region II the increase in the glass transition temperatures is a function of only the coordination number of the modifiers.¹⁰ This explains why the silver phosphates have such low T_g s, because the coordination number for silver in these glasses is around 3.5,⁵⁵ but following this logic lithium phosphates should have T_g s slightly higher than the silver phosphates, since the coordination number of lithium is approximately 4^{56–58} and the cesium phosphates should have the highest T_g s, as the coordination number for Cs is around 6,²² but this does not agree with the experimental results. While knowing the concentration of Q^n species in the glass surely provides a good description of its structure, the picture is not complete. For example, one can use the connectivity between neighbouring Q^n units to have a more comprehensive view of the network. Following the nomenclature proposed by Witter *et al.*,⁵⁹ the connectivity of a given tetrahedron is given by $Q^{n_i j k}$, where the n denotes the number of bridging oxygens in the phosphate tetrahedron and the i , j , and k superscripts

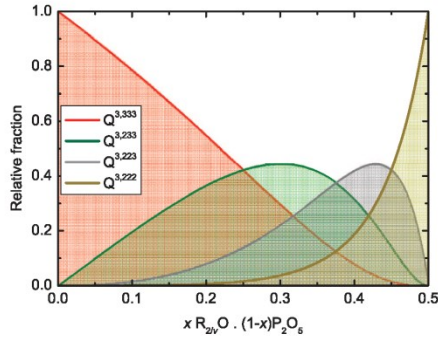


FIG. 2. Connectivity of $Q^{3,ijk}$ species in a binary phosphate glass as predicted by a random spatial distribution of the different species as a function of glass composition. The i , j , and k superscripts represent the number of bridging oxygens of the adjacent tetrahedra.

describe the number of bridging oxygens of the tetrahedra connected to the original tetrahedron. For binary lithium ultraphosphates^{60,61} and calcium pyrophosphates⁶¹ the experimental data are most accurately described by a simple random distribution, as exemplified in Figures 2 and 3.

Note that in Figure 3 the fraction of Q^2 units connected to other two Q^2 units ($Q^{2,22}$) increases steeply for $x \geq 0.1$. If the observed deviation is in fact associated with these linear phosphate segments, it would suggest that there are some constraints that are not taken into account only with the short-range chemical bonds.

III. MEDIUM-RANGE TOPOLOGICAL CONSTRAINTS

We raise the question for the origin of the excess constraints, arguing that they arise from medium-range interactions in the glass network. These could be, for example, sterical hindrance which can be associated with, e.g., packing density, chain length, or clustering. This can be exemplified using the $xAgX \cdot (1-x)AgPO_3$ glass forming systems, with

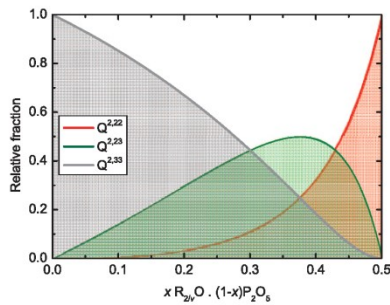


FIG. 3. Connectivity of $Q^{2,ij}$ species in a binary phosphate glass as predicted by a random spatial distribution of the different species as a function of glass composition. The i and j superscripts represent the number of bridging oxygens of the adjacent tetrahedra.

$X = Cl, Br, \text{ and } I$. The structure of such glasses has been extensively studied^{39,62–73} because of their potential applicability as solid-state conductor. Our interest in this system comes from the fact that the phosphate speciation is effectively independent of halide concentration up to $x = 0.5$,^{39,63,64,66–68,73} meaning that in this compositional range the phosphate speciation is predominantly Q^2 .

First we need to count the number of constraints for the reference glass system $xAg_2O \cdot (1-x)P_2O_5$. We take Eq. (4), which only models the phosphate network constraints and add the unknown number of constraints associated with the Ag^+ ions at the metaphosphate composition, K_{Ag} , to get Eq. (5),

$$n(x, K_{Ag}) = (2 \times X_{BO}(x)) + (3 \times X_{Q3}(x)) + (1 \times X_{Q2}(x)) + (K_{Ag} \times X_{Ag}(x)), \quad (5)$$

where X_{Ag} is the fraction of silver ions. We have that¹⁰

$$X_{BO}(x) = \frac{3 - 4x}{6 - 3x}, \quad (6)$$

$$X_{Q3}(x) = \frac{1 - 2x}{6 - 3x}, \quad (7)$$

$$X_{Q2}(x) = \frac{x}{6 - 3x}, \quad (8)$$

$$X_{Ag}(x) = \frac{2x}{6 - 3x}. \quad (9)$$

Therefore,

$$n(x, K_{Ag}) = 2 \left(\frac{3 - 4x}{6 - 3x} \right) + 3 \left(\frac{1 - 2x}{6 - 3x} \right) + \frac{x}{6 - 3x} + K_{Ag} \left(\frac{2x}{6 - 3x} \right), \quad (10)$$

$$\therefore n(x, K_{Ag}) = \frac{9 - (13 - 2K_{Ag})x}{6 - 3x}. \quad (11)$$

As we are interested in the metaphosphate composition, $x = 0.5$,

$$n(0.5, K_{Ag}) = \frac{2.5 + K_{Ag}}{4.5}. \quad (12)$$

Substituting Eq. (12) into Eq. (3) and, as the reference composition is vitreous P_2O_5 , $n(x_R) = 3/2$ and $T_g(x_R) = 590$ K. Experimental data for the glass transition temperature of silver metaphosphate show a relative large scatter, as can be seen in Figure 1; therefore, we average out the values and consider $T_g(0.5) \approx 449$ K (with a standard deviation of 18 K), giving us

$$\frac{2.5 + K_{Ag}}{4.5} = 3 - \left(\frac{590}{449} \times \frac{3}{2} \right), \quad (13)$$

$$\therefore K_{Ag} = 2.13. \quad (14)$$

This means that, on average, each silver ion contributes 2.13 bond constraints at the metaphosphate composition. We also took the highest (487 K⁴⁹) and lowest (417 K^{30,32}) reported

$T_g(0.5)$ values to estimate the upper and lower bound of K_{Ag} , resulting in $2.82 \leq K_{Ag} \leq 1.45$.

The backbone of the $xAgX_{(1-x)}AgPO_3$ glasses is formed by these silver-constrained phosphate chains. The chemical composition of these glasses can be rewritten as $(0.5-y)Ag_2O \cdot (0.5-y)P_2O_5 \cdot (2y)AgX$. It is clear that $y = x/2$, thus the fractions of chemical species in these glasses are given by

$$X_{Q2}(y) = \frac{0.5 - y}{4.5 - 5y}, \quad (15)$$

$$X_X(y) = \frac{2y}{4.5 - 5y}, \quad (16)$$

$$X_{AgP}(y) = \frac{1 - 2y}{4.5 - 5y}, \quad (17)$$

$$X_{AgX}(y) = \frac{2y}{4.5 - 5y}, \quad (18)$$

$$X_{BO}(y) = \frac{1 - 6y}{4.5 - 5y}, \quad (19)$$

where X_{AgX} are the silver ions bonded to the halide and X_{AgP} are the silver ions bonded to the phosphate chains. This differentiation is important since the silver halides do not interact directly with the phosphate network but increase the mean distance between chains,^{39,63,64,66-68,73} acting akin to solvent molecules in a polymeric solution. Hence, only the phosphate-bonded silver ions should contribute with bond constraints, and the number of atomic constraints can be calculated as follows:

$$n(y) = (2 \times X_{BO}(y)) + X_{Q2}(y) + (K_{Ag} \times X_{AgP}(y)). \quad (20)$$

Here, we calculated the number of atomic constraints for the $xAgX_{(1-x)}AgPO_3$ glasses with experimental data for $X = Cl$,⁴¹ Br ,⁴¹ and I ^{29-34,36,37,41,44,45,51,74-76} and plotted it as a function of composition in Figure 4. For reference, Eq. (20) is also plotted with the average and upper and lower bounds for K_{Ag} .

As evident in Figure 4, the $xAgX_{(1-x)}AgPO_3$ ($X = Cl, Br, I$) glasses seem to lose fewer constraints with increasing x than expected from the structural analysis when relying purely on the temperature-dependent constraint theory, independently from the number of constraints each silver atom adds to the phosphate chain. As stated above, the connectivity of the phosphate tetrahedra does not change as the concentration of silver halides increases, meaning that there is no formation of Q^1 groups and that the decrease in the atomic constraints should be only due to the substitution of phosphates for halides (Eq. (20)). Nonetheless, there seems to be some change in the structure of these glasses to account for these excess constraints. According to a very thorough study by Novita *et al.*³⁹ there is evidence from Raman and IR measurements that, as the halide concentration increases, the overall topology of the phosphate network gradually evolves from long chains to a mixture of large and small rings. There are some marked differences between chain-like and ring-like configurations, and that has been a topic of great inter-

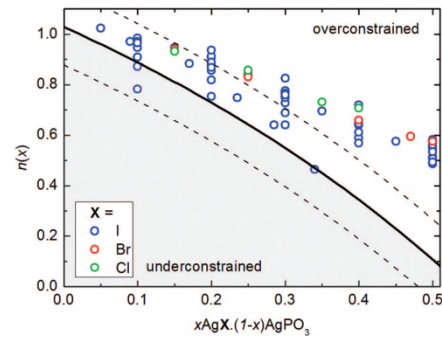


FIG. 4. Number of atomic constraints $n(x)$ as a function of composition for $xAgX_{(1-x)}AgPO_3$ glasses with $X = Cl, Br, I$. The solid line is given by Eq. (20) with $K_{Ag} = 2.13$, while the dashed lines represent the upper and lower bounds ($K_{Ag} = 2.82$ and 1.45 , respectively).

est in polymer science for some 30 years.⁷⁷⁻⁸⁶ Ring polymers exhibit smaller radius of gyration^{78,79,81,84} and smaller specific volume⁸² when compared with linear polymers of the same polymerization degree. This provides an explanation not only to the observed decrease in the molar volume of $xAgI_{(1-x)}AgPO_3$ glasses^{33,39} but also to the origin of the excess constraints. As the rings pack more efficiently, we suggest that steric effects from neighbouring rings are not negligible, especially as the topology moves towards a more ring-like configuration.

IV. CONCLUSIONS

The constraint theory of glass topology of Phillips and Thorpe inaugurated a new way of thinking about the glass network. The addition of temperature-dependent constraints by Gupta and Mauro enabled qualitative and often semi-quantitative prediction of compositional trends of properties of oxide and non-oxide glasses. We propose that one of the reasons of the disagreement between theory and measurement is the medium-range constraints that are not taken into the calculations, since the theory only counts short-range bond constraints. We show that these medium-range constraints, which may originate from chain segments or tight-packed rings, can provide an explanation as to why we measure some glass systems as under- or overconstrained.

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2.3. Decoupling of Constraint Counting

As seen previously, the Temperature Dependent Bond Constraint Theory certainly has collected successes predicting the glass transition temperature, fragility and surface hardness of certain select glass systems^{48, 72, 73, 75, 79, 81–85, 118, 185–189}, it can be further developed in understanding how the short range and intermediate range interactions could be better modeled. One characteristic of the current form of the TBCT is its strong link to the glass melt viscosity through the configurational entropy $S_c(x)$ in Adam and Gibbs formulation⁴⁸. While such association has been used as the basis for its mathematical derivation^{48, 77, 190–192}, there has been no test of whether or not the number of constraints when calculated from viscosity data agree with the short-range counting originally proposed by Mauro and coworkers^{48, 85}. The alkali borate glass system was a perfect composition to try and test such connection, because we could use the bond constraint analysis of Mauro and Gupta⁸⁵ together with the plethora of good viscosity experimental data available in the literature. Perhaps unsurprisingly we found that the number of constraints calculated from viscosity data departs quite strongly from the short range counting¹⁹³, which we correlate with Gupta and Mauro's assumption that both the number of degenerate configurations per floppy mode $\Omega(x)$ and the parameter $B(x)$ of the Adam and Gibbs equation (related to the energy barrier for reorientation of the cooperative rearranging regions^{70, 194}) should be independent of glass composition. Using the MYEGA equation¹⁹¹ to fit the viscosity data we find that as the alkali concentration increases the ration between the degeneracy of the broken and intact constraints. We also find that the MYEGA parameter $K(x)$ shows a strong change with composition which cannot be uniquely related to the degeneracy, indicating that there might be a compositional dependence also in the value of $B(x)$. Similar evidence was also found in binary sodium silicate glassy systems, where $B(x)$ appears to be constant for glasses with more than 25 mol% of Na_2O while strongly increasing as the chemical composition is enriched in silica. These results suggest that the choice of the reference composition needed to perform the glass transition temperature estimates from the Temperature Dependent Bond Constraint Theory^{48, 85} carries a large importance, as the calculation requires the values of $B(x)$ and $\Omega(x)$ to be relatively constant throughout the whole analyzed compositional range. It also puts forward the notion that viscosity data could be used as a tool to study constraints which act beyond the first coordination shell of the individual atoms.

2.3.1. Floppy Mode Degeneracy And Decoupling Of Constraint Predictions In Super-Cooled Borate And Silicate Liquids

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The theory of temperature-dependent topological constraints has been used to successfully explain the compositional dependence of glass properties for oxide and non-oxide compositions. It relates the number of topological degrees of freedom with the glass transition temperature through the configurational entropy of the system. Based on this, we estimated the number of degrees of freedom directly from viscosity measurements of binary alkali borate and silicate glasses. Both approaches exhibit a strong decoupling, which we suggest can be traced to the presence of medium- and long-range constraints that are not taken into account by bond constraint counting. The observed variation of the energy barrier for structural rearrangement and floppy mode degeneracy also corroborate our interpretation. We provide evidence that the degeneracy of floppy modes changes with chemical composition and that the parameter $K(x)$ of the MYEGA viscosity equation could be used to assess changes in the medium-range order.

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Floppy mode degeneracy and decoupling of constraint predictions in super-cooled borate and silicate liquids

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The theory of temperature-dependent topological constraints has been used to successfully explain the compositional dependence of glass properties for oxide and non-oxide compositions. It relates the number of topological degrees of freedom with the glass transition temperature through the configurational entropy of the system. Based on this, we estimated the number of degrees of freedom directly from viscosity measurements of binary alkali borate and silicate glasses. Both approaches exhibit a strong decoupling, which we suggest can be traced to the presence of medium- and long-range constraints that are not taken into account by bond constraint counting. The observed variation of the energy barrier for structural rearrangement and floppy mode degeneracy also corroborate our interpretation. We provide evidence that the degeneracy of floppy modes changes with chemical composition and that the parameter $K(x)$ of the MYEGA viscosity equation could be used to assess changes in the medium-range order.

Keywords: glass, topological constraint theory, borates, silicates, viscosity

INTRODUCTION

The theory of “topological constraints” has drawn significant attention for the prediction of specific properties of glassy materials (Phillips, 1979; Phillips and Thorpe, 1985; Gupta and Mauro, 2009; Mauro et al., 2009a; Smedskjaer et al., 2010; Wondraczek et al., 2011). It relates atomistic potentials and spatial relations between constituents of the glass to the ensemble’s degrees of freedom and the average number of atomic bond constraints, respectively. An estimate of the number of constraints can be obtained via the Adam–Gibbs equation (Adam and Gibbs, 1965), which relates the viscosity of a liquid with its configurational entropy:

$$\log_{10}\eta(T, x) = \log_{10}\eta_{\infty}(x) + \frac{B(x)}{T \cdot S_c(T, x)} \quad (1)$$

where $\eta_{\infty}(x)$ is the viscosity of the liquid at infinite temperature, $B(x)$ corresponds to the energy barrier, which opposes the rearrangement of the melt structural units (Russell et al., 2003) and $S_c(T, x)$ is the configurational entropy of the melt. The configurational entropy can, in principle, be determined from calorimetric (Richet et al., 1993) or electrochemical measurements (Jordanov et al., 2012) and is calculated from Eqs 2–4 (Richet, 1984, 2009; Richet et al., 1993).

$$S_c(T, x) = S_c(T_g, x) + \int_{T_g}^T \frac{C_p^{\text{conf}}(x)}{T} dT \quad (2)$$

$$S_c(T_g, x) = \Delta S_f + \int_0^{T_m} \frac{C_p^{\text{crystal}}(x)}{T} dT + \int_{T_m}^{T_g} \frac{C_p^{\text{liquid}}(x)}{T} dT + \int_{T_g}^0 \frac{C_p^{\text{glass}}(x)}{T} dT \quad (3)$$

$$C_p^{\text{conf}}(x) = C_p^{\text{liquid}}(x) - C_p^{\text{glass}}(T_g) \quad (4)$$

where the difference in heat capacity between glassy state and super-cooled liquid state is typically taken as the configurational heat capacity $C_p^{\text{conf}}(x)$ (Richet et al., 1986). In reality, the experimental determination of $S_c(T, x)$ is problematic at best (Sipp et al., 1997). So, while the Adam–Gibbs equation successfully links the thermodynamic state of a liquid with its dynamic properties, its practical application is restricted by the difficulties arising from the experimental determination of all required calorimetric data (Richet, 2009).

Recently, Mauro et al. (2009b) proposed a new equation to describe the viscosity of liquids, which is based on the Adam–Gibbs approach, the energy landscape analysis of Naumis (2006) and the temperature-dependent constraint model of Gupta and Mauro (2009) (Mauro et al., 2009a). The model states that temperature-induced changes in the glass topology are related to changes in the number of atomic constraints relative to the number of atomic degrees of freedom. The new equation postulates a link between the configurational entropy of the liquid and its topological degrees of freedom per atom, $f(T, x)$:

$$S_c(T, x) = f(T, x) Nk \ln \Omega \quad (5)$$

where N is the number of atoms, k is Boltzmann’s constant, and Ω is the number of degenerate configurations per floppy mode (Mauro et al., 2009b). Furthermore, the authors consider that the network constraints exist in a simple two-state system: the constraints are either intact or broken. The energy difference between both states is given by $H(x)$ (Mauro et al., 2009b):

$$f(T, x) = 3 \cdot \exp\left(-\frac{H(x)}{kT}\right) \quad (6)$$

Rearranging Eq. 1 with $K(x) = B(x)/3Nk\ln\Omega$ and $C(x) = H(x)/k$, the MYEGA equation is obtained (Mauro et al., 2009b):

$$\log_{10}\eta(T, x) = \log_{10}\eta_{\infty}(x) + \frac{K(x)}{T} \cdot \exp\left(\frac{C(x)}{T}\right) \quad (7)$$

Equation 7 can be rewritten as a function of the glass transition temperature $T_g(x)$ and the fragility index $m(x)$ (Angell, 1995) assuming that $\log\eta_{\infty}(x) = -3 [\log(\text{Pa} \cdot \text{s})]$ (Zheng et al., 2011):

$$\log_{10}\eta(T, x) = -3 + 15 \cdot \frac{T_g(x)}{T} \cdot \exp\left[\left(\frac{m(x)}{15} - 1\right) \cdot \left(\frac{T_g(x)}{T} - 1\right)\right] \quad (8)$$

This equation provides a versatile tool, which allows for the determination of the glass transition temperature, the kinetic fragility of the melt and the viscosity parameters $K(x)$ and $C(x)$ from viscosity data. Substituting $C(x)$ in Eq. 6 one can calculate the number of degrees of freedom per atom from viscosity:

$$f_{\text{visc}}(T, x) = 3 \cdot \exp\left(-\frac{C(x)}{T}\right) \quad (9)$$

NUMBER OF TOPOLOGICAL DEGREES OF FREEDOM

The temperature-dependent constraint theory of Gupta and Mauro (2009) provides another way of calculating the number of atomic degrees of freedom from experimental data (Mauro et al., 2009a). Starting with the Adam–Gibbs equation (Eq. 1), for two different but similar systems x and w at their glass transition temperature, the equilibrium viscosity should be equal to 10^{12} Pa · s, resulting in the following equality:

$$\frac{B(x)}{T_g(x) \cdot S_c(T_g(x), x)} = \frac{B(w)}{T_g(w) \cdot S_c(T_g(w), w)} \quad (10)$$

Assuming that the variation of the energy barrier is independent on chemical composition, $B(x) \approx B(w)$, and using Eq. 5 one gets:

$$\frac{T_g(w)}{T_g(x)} = \frac{S_c(T_g(x), x)}{S_c(T_g(w), w)} = \frac{f(T_g(x), x)}{f(T_g(w), w)} \quad (11)$$

In order to test if the number of atomic degrees of freedom calculated from viscosity (Eq. 9) and the Bond Constraint Theory (Eq. 11) coincide, we took viscosity data for B_2O_3 , $x\text{Na}_2\text{O} \times (1-x)\text{B}_2\text{O}_3$, and $x\text{Li}_2\text{O} \times (1-x)\text{B}_2\text{O}_3$ glasses and fitted with Eqs 7 and 8 assuming $\log\eta_{\infty}(T, x) = -3$. The results are shown in Table 1.

Considering that the relative number of degrees of freedom [given by $f(T_g(x), x)/f(T_g(w), w)$] is the same for both approaches, Eqs 9 and 11 can then be combined as:

$$\frac{f(T_g(x), x)}{f(T_g(w), w)} = \frac{T_g(w)}{T_g(x)} = \frac{\exp\left(-\frac{C(x)}{T_g(x)}\right)}{\exp\left(-\frac{C(w)}{T_g(w)}\right)} \quad (12)$$

Taking vitreous B_2O_3 as a reference composition, $T_g(w) = 522.9$ K [see Table 1; this temperature is somewhat lower than the one reported by Mauro et al. (2009a)], $C(w) = 557$ K from Table 1 and $f(T_g(w), w) = 3/5$ (Mauro et al., 2009a), then the comparison with the binary alkali glasses becomes straightforward and the results are found in Figures 1 and 2.

Interestingly, in Figure 1, we see that the number of floppy modes calculated from viscosity measurements has a stronger dependence on the chemical composition than the one calculated from glass transition temperature data. Figure 2 illustrates this mismatch very well and we see that both alkali borate glasses follow the same trend.

DEGENERACY AND DECOUPLING OF CONSTRAINT PREDICTIONS

From Figures 1 and 2, the experimental data suggest that the number of degrees of freedom from viscosity and the BCT diverge significantly. Recalling Eq. 5, we see that the configurational entropy is a function of the atomic degrees of freedom, the number of atoms and the degeneracy of each floppy mode. Equation 11 assumes that the size of the system and the floppy mode degeneracy can be considered constant as the chemical composition changes. While the number of atoms in the system may vary slowly enough to be considered constant [as the molar volume of sodium borate glasses does not exhibit a strong compositional variation (Berke-meier et al., 2005)], the floppy mode degeneracy has to be analyzed more carefully. As stated above, Mauro et al. (2009a) modeled the bond constraints as a simple two-state system with the energy difference between the broken and intact constraints given by $H(x)$ and the number of topological degrees of freedom given by Eq. 6. This simple system is represented schematically in Figure 3A.

The fraction of bond constraints that are either broken or intact can then be calculated through the Boltzmann distribution (Landau and Lifshitz, 1980):

$$\frac{N_i}{N} = \frac{g_i \exp\left(-\frac{E_i}{kT}\right)}{Z(T)} \quad (13)$$

where N_i is the number of bond constraints with energy E_i , N is the total number of bond constraints, g_i is the degeneracy of the state of energy E_i (or, in other words, the number of different states with the same energy E_i), and $Z(T)$ is the partition function, given by:

$$Z(T) = \sum_i g_i \exp\left(-\frac{E_i}{kT}\right) \quad (14)$$

It is important to note that this calculation of the fractions of intact and broken constraints requires that the constraint breakage to not be a step-function of the temperature, which is in line with recent MD simulations (Bauchy and Micoulaut, 2011). From Figure 3A, we have that the intact bond constraints have ground energy $E_g(x)$ and the broken constraints have an energy of $E_g(x) + H(x)$. Thus, the relation between the number of broken and intact constraints is given by:

$$\frac{N_b(T, x)}{N_i(T, x)} = \frac{g_b(T, x) \exp\left(-\frac{E_g(x) + H(x)}{kT}\right)}{g_i(T, x) \exp\left(-\frac{E_g(x)}{kT}\right)} \quad (15)$$

Table 1 | Parameters of Eqs 7 and 8 as a function of chemical composition for binary $x\text{Na}_2\text{O}-(100-x)\text{B}_2\text{O}_3$ and $x\text{Li}_2\text{O}-(100-x)\text{B}_2\text{O}_3$.

Composition $x\text{M}_2\text{O}-(100-x)\text{B}_2\text{O}_3$ (mol%)	$K(x)$ (Eq. 7)	$C(x)$ (Eq. 7)	m (Eq. 8)	T_g (Eq. 8)	Reference
0	2653	557	31.3	522.9	Sasek et al. (1984), Shartis et al. (1953a,b), Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Volarovich and Tolstoi (1934), Rabinovich (1942), Yamate and Kadogawa (1984)
M = Na					
3	2022	763	36.0	545.5	Shartis et al. (1953a,b), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962); Nemilov (1966)
4.2	2146	783	35.7	567.9	Sasek et al. (1984), Yamate and Kadogawa (1984)
5.2	1586	981	40.5	577.8	Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Nemilov (1966), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
6.3	1174	1245	45.7	607.5	Shartis et al. (1953a,b), Volarovich and Tolstoi (1934), Li et al. (1960), Li et al. (1962), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
7.8	1706	975	39.7	591.2	Sasek et al. (1984), Nemilov (1966)
10	1056	1372	47.8	627.3	Shartis et al. (1953a,b), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962)
10.9	1166	1321	46.4	631.0	Matusita et al. (1980); Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984)
13.5	1299	1301	45.2	647.1	Nemilov (1966)
14.6	857	1704	52.3	685.7	Sasek et al. (1984) Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Yamate and Kadogawa (1984), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973), Stolyar et al. (1984), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977)
15.7	963	1586	50.3	674.7	Shartis et al. (1953a), Shartis et al. (1953b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Nemilov (1966), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
18	1163	1512	47.8	691.1	Sasek et al. (1984), Nemilov (1966), Jenckel (1935)
19.6	565	2123	59.3	719.6	Shartis et al. (1953a,b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Nemilov (1966)
20.1	638	2052	57.5	723.9	Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Volarovich and Tolstoi (1934), Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977), Jenckel (1935)
24.1	556	2186	59.8	732.4	Sasek et al. (1984), Volarovich and Tolstoi (1934), Nemilov (1966), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977)
24.5	556	2205	59.8	737.6	Shartis et al. (1953a,b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962), Nemilov (1966), Visser and Stevels (1972a,b), Stevels (1973), Stolyar et al. (1984), Jenckel (1935)
27.2	443	2398	63.4	743.3	Sasek et al. (1984), Nemilov (1966), Stolyar et al. (1984)
28.7	623	2121	58.2	737.2	Shartis et al. (1953a,b), Stolyar et al. (1984), Jenckel (1935)
29.6	475	2326	62.3	738.5	Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Nemilov (1966), Visser and Stevels (1972a,b), Stevels (1973), Jenckel (1935)

(Continued)

Table 1 | Continued

Composition $xM_2O \cdot (100-x)$ B_2O_3 (mol%)	$K(x)$ (Eq. 7)	$C(x)$ (Eq. 7)	m (Eq. 8)	T_g (Eq. 8)	Reference
33.4	305	2627	68.8	733.1	Sasek et al. (1984), Shartis et al. (1953a,b), Volarovich and Tolstoi (1934), Rabinovich (1942), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984), Jenckel (1935), Danek and Licko (1981)
M = Li					
2	1711	916	39.1	569.4	Shartis et al. (1953a,b), Yamate and Kadogawa (1984)
6.3	1211	1245	45.4	613.8	Shartis et al. (1953a,b), Matusita et al. (1980), Visser and Stevels (1972a,b), Stevels (1973)
9.9	975	1470	49.4	642.0	Shartis et al. (1953a,b), Yamate and Kadogawa (1984)
13.9	656	1941	56.6	699.9	Shartis et al. (1953a,b), Yamate and Kadogawa (1984), Visser and Stevels (1972a,b), Stevels (1973)
14.9	441	2312	63.0	722.4	Matusita et al. (1980), Visser and Stevels (1972a,b), Stevels (1973)

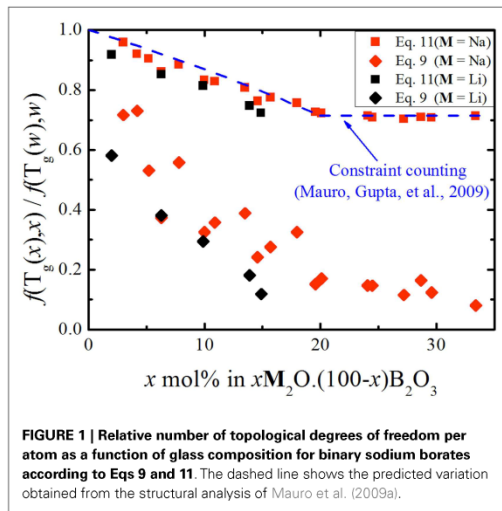


FIGURE 1 | Relative number of topological degrees of freedom per atom as a function of glass composition for binary sodium borates according to Eqs 9 and 11. The dashed line shows the predicted variation obtained from the structural analysis of Mauro et al. (2009a).

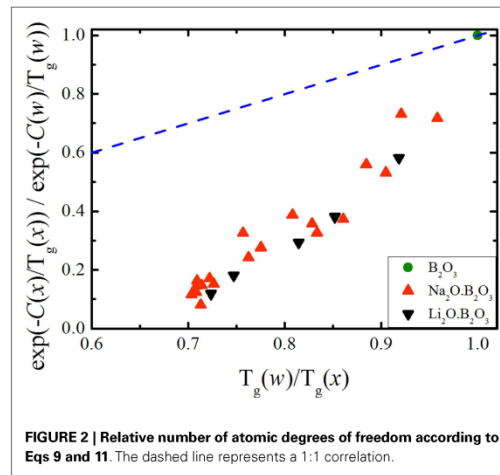


FIGURE 2 | Relative number of atomic degrees of freedom according to Eqs 9 and 11. The dashed line represents a 1:1 correlation.

where $N_b(T, x)$ is the number of broken bond constraints, $N_i(T, x)$ is the number of intact bond constraints, $g_b(T, x)$ is the degeneracy of the broken state, and $g_i(T, x)$ is the degeneracy of the intact state. Eq. 15 simplifies to:

$$\frac{N_b(T, x)}{N_i(T, x)} = \frac{g_b(T, x)}{g_i(T, x)} \exp\left(-\frac{H(x)}{kT}\right) \quad (16)$$

The number of floppy modes is equal to the number of broken constraints, $N_b(T, x) = f(T, x)$, and according to Gupta and Mauro (2009) the number of floppy modes is also given by $f(T, x) = d - n(T, x)$, where d is the dimensionality of the network and $n(T, x)$ is the number of intact bond constraints.

In our case $d = 3$, resulting in $n(T, x) = N_i(T, x) = 3 - f(T, x)$. As $C(x) = H(x)/k$, Eq. 16 can be rewritten as:

$$\frac{g_b(T_g(x), x)}{g_i(T_g(x), x)} = \frac{f(T_g(x), x)}{3 - f(T_g(x), x)} \exp\left(\frac{C(x)}{T_g(x)}\right) \quad (17)$$

By taking values of $C(x)$ and using Eq. 11 to calculate $f(T_g(x), x)$, as it gives the best agreement with structural data, we can estimate the relative degeneracy of states as a function of chemical composition (Figure 3B).

As the glasses get richer in alkali (i.e., more polymerized), the floppy modes get more degenerate in relation to the intact bond constraints. This might provide an explanation for the transition in the type of floppy mode, which controls the glass transition temperature in these alkali borate glasses (Mauro et al., 2009a).

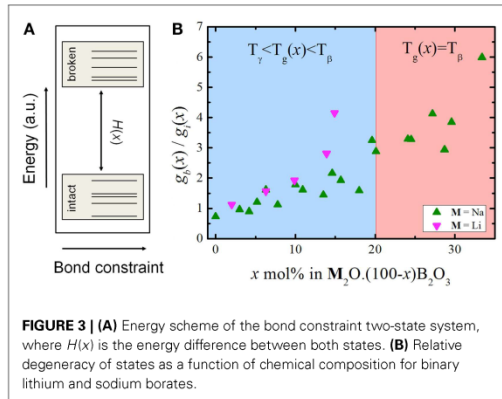


FIGURE 3 | (A) Energy scheme of the bond constraint two-state system, where $H(x)$ is the energy difference between both states. **(B)** Relative degeneracy of states as a function of chemical composition for binary lithium and sodium borates.

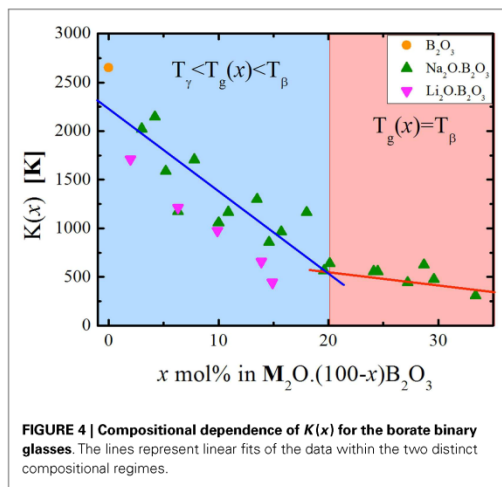


FIGURE 4 | Compositional dependence of $K(x)$ for the borate binary glasses. The lines represent linear fits of the data within the two distinct compositional regimes.

The compositional changes might render the intact B–O–B angular constraints less degenerate and we interpret this as a reduction in the angular flexibility, meaning that as the degeneracy decreases these constraints become more rigid. At some compositional range, these transitions become so unlikely that it becomes more probable to break other constraints, in this case, the O–B–O angular constraint. The transition between floppy modes is very discernible independently of how the number of topological degrees of freedom is calculated (Figure 1). This also correlates with the variation of $K(x)$ with the chemical composition, as can be seen in Figure 4.

According to Mauro et al. (2009b), $K(x)$ is written as:

$$K(x) = \frac{B(x)}{3Nk \ln \Omega} \quad (18)$$

Therefore, any change in $K(x)$ means that either $B(x)$ and/or Ω are changing. If the assumption that $B(x) \approx B(w)$ used in the

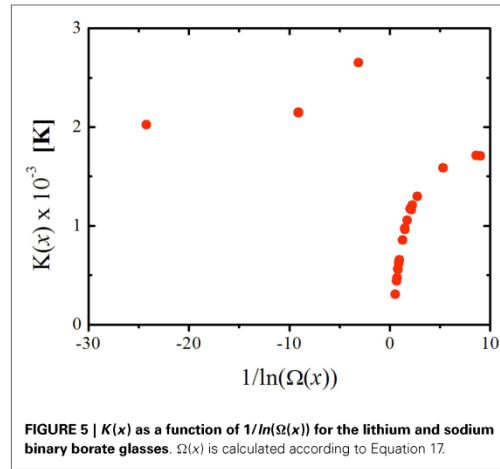


FIGURE 5 | $K(x)$ as a function of $1/\ln(\Omega(x))$ for the lithium and sodium binary borate glasses. $\Omega(x)$ is calculated according to Equation 17.

derivation of Eq. 11 is correct, then plotting the values of $K(x)$ as a function of $1/\ln(\Omega(x))$ should result in a straight line passing through the origin, but as we can see from Figure 5 this is far from what we get. Therefore, not only the degeneracy is causing $K(x)$ to change with composition but also the energy barrier of structural rearrangement, $B(x)$. From Eqs 1 and 7 we get that, at $T = T_g$:

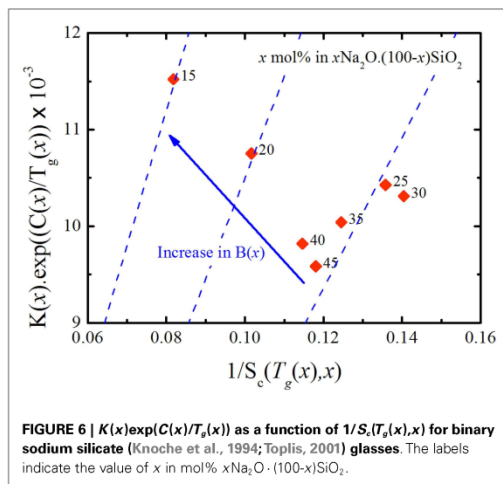
$$\frac{B(x)}{S_c(T_g(x), x)} = K(x) \cdot \exp\left(\frac{C(x)}{T_g(x)}\right) \quad (19)$$

Thus, plotting $K(x) \exp(C(x)/T_g(x))$ as a function of $1/S_c(T_g(x), x)$ should yield a straight line passing through the origin with a constant, positive slope of $B(x)$ for all glasses of the same “family.” Analyzing the available thermodynamic and viscosity data for $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ glasses (Knoche et al., 1994; Toplis, 2001) resulted in the graph in Figure 6, where one can see that even though $B(x)$ appears to be constant for $x \geq 0.25$, it increases as the glass compositions get richer in silica. The observed change in the behavior of $B(x)$ at $x \approx 0.2$ is consistent with the glass network transitioning from stressed-rigid to floppy. Such transition has already been reported in experimental (Vails et al., 2005) and MD simulations (Bauchy and Micoulaut, 2011).

Adam and Gibbs (1965) demonstrated that $B(x)$ is given by:

$$B(x) = \frac{n_p \Delta\mu(x) S_c^*(x)}{k} \quad (20)$$

where n_p is the number of particles in the system, $\Delta\mu(x)$ is the average energy barrier each rearranging region has to overcome during cooperative motion, and $S_c^*(x)$ is the configurational entropy of the smallest rearranging region. As argued before, the number of particles in the system is considered to be constant, meaning that the observed variations in $K(x)$ are due to changes in $\Delta\mu(x)$ and $S_c^*(x)$. These two parameters are sensitive to changes in the medium- and long-range orders, as they are associated with cooperative rearranging regions (CRRs); thus, we suggest that the



observed variation of $K(x)$ as a function of composition stems from the changes in the CRRs, which can only change if the floppy modes enable these regions to become more or less flexible. This line of reasoning suggests that the properties of the CRRs are deeply connected to the number and types of floppy modes in the glass network, as they should dictate the possible rearrangements a certain region can reach.

As $B(x) \neq B(w)$, one should observe a decoupling on the values of topological degrees of freedom per atom estimated from viscosity and bond constraint counting. We propose that the main reason for this decoupling is that while the viscosity reflects the behavior of the whole system, combining the responses of short-, medium-, and long-range interactions, the bond constraints are, by their own definition, restricted to short-range interactions. It is known that medium-range interactions affect the measured viscosity of polymers, with the molecular weight of side groups (Rogers and Mandelkern, 1957; Gargallo et al., 1987, 1988) and the shape of chains (Gonzalez et al., 1988; Hur et al., 2011; Khalyavina et al., 2012) having significant influence even though the covalent chemical bonds that make the backbone of the chains stay constant; and recent evidence points that the same effects may be present in inorganic oxide glasses (Rodrigues and Wondraczek, 2013). The coulombic interactions between the modifiers and the non-bridging oxygens extend beyond its first coordination shell, and it has been shown that they are a major part of the constraints present in phosphate glasses (Hermansen et al., 2014; Rodrigues and Wondraczek, 2014; Rodrigues et al., 2014), so they might also have an effect here. The apparent influence of the medium range also ties with the possible differentiability of the floppy modes. When counting, the constraints are either intact or broken and two floppy modes are considered the same even if their surroundings are very different. For example, in the binary alkali borate glasses, when considering the breakage of the angular constraints of the bridging oxygens, each trigonally coordinated boron has three floppy modes regardless of the fact that it may be bonded to three other trigonal borons or three tetragonal borons. But these two

different configurations may very well have different configurational entropies associated, influencing the CRRs and, ultimately, the viscosity of the system. This may indicate that the parameter $K(x)$ can be used to probe changes in the medium-range order of super-cooled liquids as a function of chemical composition.

CONCLUSION

In this paper, the viscosity of binary alkali borates and silicates was used to estimate the number of topological degrees of freedom as a function of glass composition. The number of floppy modes estimated from viscosity decouples from the values, which are obtained by bond constraint counting. We suggest that the origin of this decoupling is due to the difference in scale: while viscosity covers the whole system, bond constraint counting only handles short-range interactions; hence the observed inequality of $B(x)$. We provide evidence that the degeneracy of floppy modes changes with chemical composition and that the parameter $K(x)$ of the MYEGA viscosity equation could be used to assess changes in the medium-range order.

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3. SUMMARY

The aim of this work was to broaden the current understanding of the Temperature Dependent Bond Constraint Theory, addressing how short and medium range interactions affect the number of constraints while also looking at the limits of the theory's applicability.

Working with phosphate glasses allows for a straightforward model of the phosphorus network constraints, so that other effects can be more easily discerned. In review we find that the number of constraints provided by the modifiers is not determined by its coordination number but by the strength of its electrostatic interaction with the surrounding non-bridging oxygens. We also find that the presence of non-bridging oxygens dictate whether the modifier in question is found in an "isolated" site, where its coordinated chiefly by double bonded oxygens, or in a "cross-linking" site, where there are non-bridging oxygens belonging to at least two different phosphate tetrahedra; the balance of such sites is changed as the glass composition changes from pure phosphorus oxide to the metaphosphate and its fundamentally responsible for the observed increase on the glass transition temperature of these glasses above a certain threshold composition. These are short range interactions that help dictate how constrained the overall glassy network is, but there are also intermediate range effects that are non-negligible. We also find that on mixed alkali ultraphosphates the weakening of the modifier constraints can be attributed to the presence of dissimilar ions on sites immediately neighbouring any given modifier. Additionally, the silver metaphosphate – silver halide glass system was found to be overconstrained when compared with the theoretical number of constraints, and this effect is accredited to a change on the concentration ratio between phosphate chain and rings, with compositions richer in halide also having a higher concentration of phosphate rings assembling the glassy network. Finally, we argue that the TDBCT has to be judiciously applied since viscosity data implies that some of its basic assumptions are not satisfied even in simple binary oxide glasses such as alkali borates and alkali silicates.

In conclusion, the Temperature Dependent Bond Constraint Theory has achieved remarkable success modeling the compositional dependence of the glass transition temperature, surface hardness and liquid fragility of selected glass systems. Its basic tenets are easily applicable and are flexible enough to incorporate the addition of parameters that describe other effects, such as the ionic character of certain chemical bonds, or the distribution of ions on certain network sites. While this improves the theory's accuracy, it also greatly decreases its general applicability due to the addition of several parameters which are only estimable with plenty of experimental data on the system of interest.

4. ZUSAMMENFASSUNG

Die Arbeit bestand darin, das derzeitige Verständnis der Temperature Dependent Bond Constraint Theory (Temperaturabhängigen Geometrischer Bindungszwang Theorie) zu erweitern, indem untersucht wird, wie sich kurze und mittlere Wechselwirkungen auf die Anzahl von Bindungszwänge auswirken, und die Grenzen der Anwendbarkeit der Theorie erkunden werden.

Das Arbeiten mit Phosphatgläsern ermöglicht ein einfaches Modell der Phosphornetzwerkzwänge, so dass andere Effekte leichter erkannt werden können. Im Rückblick sehen wir, dass die Anzahl der Bindungszwänge, die durch die Modifikatoren zur Verfügung gestellt werden, nicht durch die Koordinationszahl, sondern durch die Kraft der elektrostatischen Wechselwirkung mit den umgebenden nicht-brückenbildeten Sauerstoffatomen bestimmt wird. Es zeigt sich auch, dass die Gegenwart von nicht-brückenbildendem Sauerstoff darüber entscheidend ist, ob der betroffene Modifikator an einer „isolierten Stelle“ zu finden ist, an der hauptsächlich doppelt gebundene Sauerstoffatome koordiniert sind oder an einer „Vernetzungsstelle“, an der sich nicht-brückenbildende Sauerstoffatome befinden, welche zu mindestens zwei unterschiedlichen Phosphattetraedern gehören; das Gleichgewicht solcher Stellen verändert sich durch die Änderung der Glaszusammensetzung von reinem Phosphoroxid zu Metaphosphat und ist grundsätzlich für die beobachteten Anstieg der Glasübergangstemperatur derjenigen Gläser verantwortlich, die eine bestimmte Zusammensetzungsschwelle überschreiten. Diese kurzen Wechselwirkungen helfen zu erklären, wie sehr das globale Glasnetzwerk eingeschränkt ist, wobei es auch mittlere Effekte gibt, welche nicht unerheblich sind. Darüber hinaus hat sich gezeigt, dass im Falle von gemischten Alkali-Ultraphosphaten die Abschwächung der Modifikatorenbindungszwänge auf das Vorkommen von unterschiedlichen Ionen zurückzuführen ist, welche sich an Stellen befinden, die unmittelbar neben einem beliebigen Modifikator liegen. Des Weiteren das Silbermetaphosphat – Silberhalogenidglassysteme wurden im Vergleich zur theoretischen Anzahl an Bindungszwänge für stark eingeschränkt befunden. Dieser Effekt wird auf einen Wechsel des Konzentrationsverhältnisses zwischen Phosphatketten und Ringen zurückgeführt. Erwähnenswert ist auch, dass Zusammensetzungen mit höherer Halogenidkonzentration auch eine höhere Konzentration an Ringen aufweisen, welche das Glasnetzwerk bilden. Schließlich wird erörtert, dass die TDBCT sorgfältig angewendet werden muss, da Viskositätsdaten andeuten, dass einige der grundlegenden Annahmen nicht erfüllt werden, selbst in einfachen binären Oxidgläsern wie z.B. Alkaliboraten oder Alkalisilikaten.

Zusammenfassend wurde mit der Temperature Dependent Bond Constraint Theory ein bemerkenswerter Erfolg bei der Modellierung der kompositorischen Abhängigkeit der Glasübergangstemperatur, der Oberflächenhärte und der Flüssigkeitsfragilität ausgewählter Glassysteme erzielt. Die grundlegenden Prinzipien sind leicht anwendbar und sind flexibel genug, um die Addition von Parametern miteinzubeziehen, welche andere Effekte

beschreiben, wie z.B. den ionischen Charakter bestimmter chemischer Verbindungen oder die Ionenverteilung an bestimmte Netzwerkstellen. Während dies die Genauigkeit der Theorie verbessert, verringert sich dadurch auch die allgemeine Anwendbarkeit aufgrund der Zunahme an einigen Parametern, die nur mit zahlreichen experimentellen Daten einschätzbar sind.

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ERKLÄRUNG ZU DEN EIGENANTEILEN DES PROMOVENDEN/DER PROMOVENDIN

Erklärung zu den Eigenanteilen des Promovenden/der Promovendin sowie der weiteren Doktoranden/Doktorandinnen als Co-Autoren an den Publikationen und Zweitpublikationsrechten bei einer kumulativen Dissertation.

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Jena, 10.08.2016

Bruno Poletto Rodrigues

EINVERSTÄNDNISERKLÄRUNG DES BETREUERS

Ich bin mit der Abfassung der Dissertation als publikationsbasiert, d.h. kumulativ, einverstanden und bestätige die vorstehenden Angaben. Eine entsprechend begründete Befürwortung mit Angabe des wissenschaftlichen Anteils des Doktoranden an den verwendeten Publikationen werde ich parallel an den Rat der Chemisch-Geowissenschaftlichen Fakultät richten.

Jena 10.08.2016

Prof. Dr. Ing. Lothar Wondraczek

ANRECHNUNG DER PUBLIKATIONSÄQUIVALENTE

Medium-range topological constraints in binary phosphate glasses, J. Chem. Phys., 138, 244507 (2013)

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Konzeption des Forschungsansatzes	X	X
Planung der Untersuchungen	X	
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Cationic constraint effects in metaphosphate glasses, J. Chem. Phys., 140, 214501 (2014)

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Konzeption des Forschungsansatzes	X	X
Planung der Untersuchungen	X	
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Vorschlag Anrechnung der Publikationsäquivalente	1.0	

Modifier constraints in alkali ultraphosphate glasses, J. Non-Cryst. Solids, 405, 12-15 (2014)

	Author 1: B. P. Rodrigues	Author 2: J. C. Mauro	Author 3: Y. Yue	Author 4: L. Wondraczek
Konzeption des Forschungsansatzes	X			X
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Schreiben des Manuskriptes	X	X	X	X
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An extended topological model for binary phosphate glasses, J. Chem. Phys, 141, 244502 (2014)

	Author 1: C. Hermansen	Author 2: B. P. Rodrigues	Author 3: L. Wondraczek	Author 4: Y. Yue
Konzeption des Forschungsansatzes	X			X
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Schreiben des Manuskriptes	X	X	X	X
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Strain-rate sensitivity of glasses, J. Non-Cryst. Solids, 404, 124-134 (2015)

	Author 1: R. Limbach	Author 2: B. P. Rodrigues	Author 3: L. Wondraczek
Konzeption des Forschungsansatzes	X		X
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Floppy mode degeneracy and decoupling of constraint predictions in super-cooled borate and silicate liquids", Front. Mater., 1, 32 (2015)

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Elasticity, deformation and fracture of mixed fluoride-phosphate glasses, J. Non-Cryst. Solids, 430, 99-107 (2015)

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Konzeption des Forschungsansatzes	X			X
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Modifier interaction and mixed-alkali effect in bond constraint theory applied to ternary alkali metaphosphate glasses, Front. Mater., 3, 25 (2016)

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DECLARATION OF AUTHORSHIP/ SELBSTÄNDIGKEITSERKLÄRUNG

I state that the entirety of this thesis is based on my own research, except where otherwise acknowledged. This corpus of work has not been previously submitted for a Ph.D. degree at this or any other university.

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Bruno Poletto Rodrigues

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

Jena, 10.08.2016

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