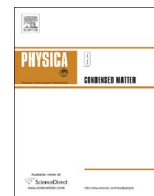




ELSEVIER

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Modifier constraint in alkali borophosphate glasses using topological constraint theory



Xiang Li^a, Huidan Zeng^{a,*}, Qi Jiang^a, Donghui Zhao^b, Guorong Chen^a, Zhaofeng Wang^c, Luyi Sun^c, Jianding Chen^a

^a Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

^b Unifrax Corporation, Niagara Falls, NY 14305, USA

^c Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA

ARTICLE INFO

Article history:

Received 3 December 2015

Received in revised form

16 August 2016

Accepted 19 August 2016

Available online 20 August 2016

Keywords:

Topological constraint theory

Modifier constraint

Phosphate glasses

Glass transition temperature

ABSTRACT

In recent years, composition-dependent properties of glasses have been successfully predicted using the topological constraint theory. The constraints of the glass network are derived from two main parts: network formers and network modifiers. The constraints of the network formers can be calculated on the basis of the topological structure of the glass. However, the latter cannot be accurately calculated in this way, because of the existing of ionic bonds. In this paper, the constraints of the modifier ions in phosphate glasses were thoroughly investigated using the topological constraint theory. The results show that the constraints of the modifier ions are gradually increased with the addition of alkali oxides. Furthermore, an improved topological constraint theory for borophosphate glasses is proposed by taking the composition-dependent constraints of the network modifiers into consideration. The proposed theory is subsequently evaluated by analyzing the composition dependence of the glass transition temperature in alkali borophosphate glasses. This method is supposed to be extended to other similar glass systems containing alkali ions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The topological constraint theory has gained extensive attention recently as it provides a knowledge-based approach to study the composition-dependent properties of glasses [1]. It was first introduced by Phillips and Thorpe, who demonstrated the relationship between the properties of a glass and the topology of the glass network [2,3]. The topology of a glass network is basically characterized by the spatial and angular invariants between the constituted polyhedra in the glass network (the average number of atomic constraints, $n(x)$) [2]. According to Phillips–Thorpe theory, the change of glass topology is closely related to atomic constraints [2]. Based on this theory, Gupta and Mauro proposed a temperature-dependent constraint model by taking into consideration the effect of temperature on the number of atomic constraints [4,5]. This model relies on counting the number of atomic constraints in the temperature range of the properties of interest. As a result, topological constraint theory was extended to calculate the physical properties of glasses, such as glass transition

temperature [4–10], fragility [4,5] and indentation hardness, based on the topology of glass networks [8–13]. Recently, Pignatelli and Smedskjaer have found relationships between the number of atomic constraints with dissolution kinetics and sub-critical crack growth, respectively [14,15]. The topological constraint theory has recently been applied to chalcogenide [4], oxide [5–7,9,13,16], and oxynitride glasses [17]. If the structural information is available, the quantitative design of glass composition for particular requirements can be achieved, such as descent of glass transition temperature for thermoforming.

It is noteworthy that both the short-range and medium-range structures contribute to the constraint of the glass network. The physical properties of the glasses are determined by the constraint of the glass network. Although network modifiers do play an important role in the network [18–22], the original theory is usually only concerned with the network formers, and it cannot distinguish the contribution of different network modifiers [5,6]. The contribution of the network formers can be estimated according to the topological structure of the glass, i.e., linear constraints from covalent or mixed-covalent bonds and angular constraints from bond angles [2]. The values of these two types of constraints are expressed to $r/2$ and $<2r-3>$ (r representing the coordination of the atom in the glass network), respectively [2]. But the

* Corresponding author.

E-mail address: hdzeng@ecust.edu.cn (H. Zeng).

contribution of the network modifiers cannot be calculated as the former, owing to the existence of ionic bonds [20,21]. Hoppe proposed that by modifying ion coordination, polyhedra in the phosphate network had a tendency to share vertices or edges with an increasing content of modifying oxide. That is, alkali ions share non-bonding oxygen to satisfy their coordination requirements at higher alkali oxide contents [23]. Hermansen et al. proposed the concept of modifying ion sub-network structures [18] based on this model [23]. Modifying ions are isolated sites below the critical concentration of modifying oxide in the phosphate network, and they crosslink with sites above the critical concentration [18]. Different values of constraint correspond to these two states. [18,19,23] Meanwhile, Rodrigues et al. successfully calculated the constraints of alkali ions in metaphosphate glasses utilizing topological constraint theory [20,21]. However, composition-dependent constraints of network modifiers have not been calculated in this way, and it is therefore interesting to examine it.

In this paper, composition-dependent constraints of network modifiers in $xR_2O(1-x)P_2O_5$ ($R=Li, Na, Cs$) glasses are studied by the topological constraint theory. Then the glass transition temperatures of $(R_2O)_{1/3}[(B_2O_3)_y(P_2O_5)_{1-y}]_{2/3}$ ($R=Li, Na, Cs$) glasses are calculated by taking both the contributions of network formers and network modifiers into consideration. In addition, the structural analysis of network formers in alkali borophosphate glasses is improved, and a significant quantity of $B^{(4)}-B^{(4)}$ linkages (about 10% in all boron atoms) are shown to be present in the glass network at a temperature higher than absolute zero [25].

2. Modifier constraints

Due to their complicated underlying structure, phosphate glasses have properties with anomalous composition-dependent trends [26]. Besides the strong effects on network formers, modifying oxides also play an important role in the forming of glass networks, which act as network modifiers in these glasses [18–22,24]. The constraint of an alkali ion in phosphate glasses is defined as δ_R ($R=Li, Na, Cs$), which is a measure of how strongly the network modifiers contribute to the rigidity of the network. Then the contribution of alkali ions to the constraint of the network (n_{mod}) can be expressed by

$$n_{mod}(x) = \delta_R \times N(R^+, x), \tag{1}$$

where $N(R^+, x)$ is the fraction of alkali ions in the network. Based on the temperature-dependent constraint model, glass transition temperature (T_g) is inversely proportional to the atomic degree of freedom (f). Therefore, one can relate T_g and f at the glass transition temperature between two glasses of similar composition as follows:

$$\frac{T_g(x)}{T_g(x_R)} = \frac{f(T_g(x_R), x_R)}{f(T_g(x), x)} = \frac{d - n_{sys}(T_g(x_R), x_R)}{d - n_{sys}(T_g(x), x)}, \tag{2}$$

where $T_g(x)$ is the glass transition temperature for a glass of chemical composition x , d is the dimensionality of the network (d is equal to 3 in glass network), and $f(T_g(x), x)$ and $n_{sys}(T_g(x), x)$ are atomic degree of freedom and atomic constraints of a glass system at glass transition temperature, respectively. Then the constraint of the composition x can be expressed using the following equation:

$$n_{sys}(x) = 3 - [3 - n_{sys}(x_R)] \frac{T_g(x_R)}{T_g(x)}. \tag{3}$$

Additionally, as the number of constraints in the glass system is basically the sum of the constraints added by the network formers (n_{net}) and the network modifiers, the constraint of a system can be

calculated by the following equation:

$$n_{sys}(x) = n_{net}(x) + n_{mod}(x) = 2 \times N(BO, x) + N(NBO, x) + 3 \times N(P^{(3)}, x) + 5 \times [N(P^{(2)}, x) + N(P^{(1)}, x) + N(P^{(0)}, x)] + \delta_R \times N(R^+, x). \tag{4}$$

There are two linear constraints at each bridging oxygen atom and one at each non-bridging oxygen atom. Three angular constraints are associated with the $P^{(3)}$ unit, and five angular constraints are associated with the $P^{(2)}$, $P^{(1)}$ and $P^{(0)}$ units. Combining Eq. (3) and Eq. (4), the value of δ_R can be expressed as a function of x . The value of x_R can be set as 0, which is the composition of vitreous P_2O_5 (there are only $P^{(3)}$ units without any network modifiers in the network), so $n_{sys}(0)=n_{net}(0)$. Then the value of δ_R can be expressed as:

$$\delta_R = \frac{n_{sys}(x) - n_{net}(x)}{N(R^+, x)} = \frac{\left\{ 3 - [3 - n_{net}(0)] \frac{T_g(0)}{T_g(x)} \right\} - n_{net}(x)}{N(R^+, x)}, \tag{5}$$

Where $T_g(0)=590$ K [6]. Using this approach, one can easily calculate the number of constraints per modifier if experimental data on the glass transition temperature is available. Using the structural model of alkali phosphate glasses, [18] the constraints of the modifier ions (Li, Na and Cs) in phosphate glasses were calculated using the experimental data of T_g [27–49], and the results are shown in Fig. 1.

It was found that the constraints of each modifier species were gradually increased with the addition of alkali oxides. It is noteworthy that the value of Li^+ is nearly the same as Na^+ with changing composition, which should be attributed to their large and similar values of charge-to-distance ratio (q/r , where q represents the electric charge of the modifier, and r is the sum of the ionic radii of O^{2-} and the modifier) [21]. The value of Cs^+ is below that of Li^+ and Na^+ because of the low value of its q/r ratio [21]. At the content of $N(R^+, x)=20\%$ (which is the composition of metaphosphate glasses), the constraints of Li^+ , Na^+ , and Cs^+ are 3, 3, and 2, respectively; the above values were demonstrated by Hermansen et al. in their recent paper [24]. It is also worth noting that the trend line increases quickly when exceeding 20%, which indicates the added alkali ions having difficulty in satisfying their coordination requirements with NBOs (the value of $N(R^+, x)$ will not increase with the addition of alkali oxides); therefore some NBOs may coordinate with more than two alkali ions [18].

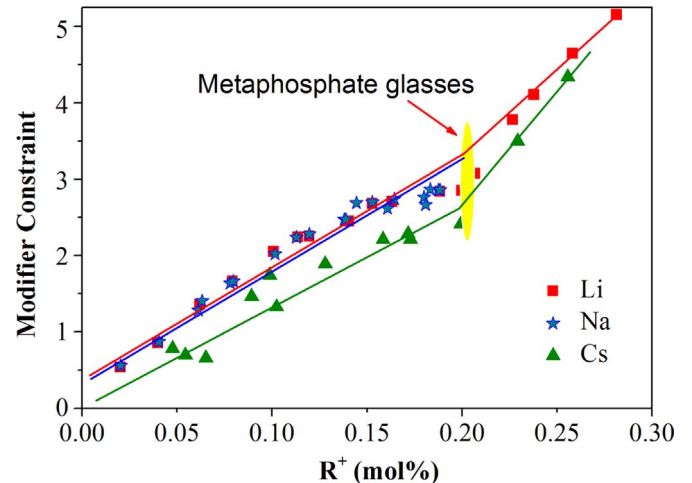


Fig. 1. Composition-dependent constraints of network modifiers in $xR_2O(1-x)P_2O_5$ ($R=Li, Na, Cs$) glasses.

Download English Version:

<https://daneshyari.com/en/article/1808169>

Download Persian Version:

<https://daneshyari.com/article/1808169>

[Daneshyari.com](https://daneshyari.com)