



Modeling the thermal poling of glasses using molecular dynamics. Part 1: Effects on glass structure



Adama Tandia^{a,*}, Mardochee Reveil^b, K. Deenamma Vargheese^a, Jian Luo^a, John C. Mauro^a, Paulette Clancy^b

^a Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA

^b Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, USA

ARTICLE INFO

Article history:

Received 12 December 2016

Received in revised form 27 January 2017

Accepted 28 January 2017

Available online xxxx

Keywords:

Glass

Thermal poling

Molecular Dynamics

Coordination numbers

ABSTRACT

Due to its ability to permanently alter key properties of glasses after melting, thermal poling is considered a promising candidate for post-melt processing of glasses. However, in order to take full advantage of this technique, a deeper understanding of the processes involved in the compositional and structural changes observed after poling is necessary. In this study, we evaluate the advantages and limitations of using Molecular Dynamics (MD) to study thermal poling. We show that MD can successfully reproduce key experimental observations related to thermal poling. Specifically, the conversion of B^{IV} to B^{III} in borosilicates with four different network modifiers is well replicated in our simulations. Moreover, our simulations reveal the coordination number of Al atoms is redistributed between the IV, V and VI coordination states. The elimination of non-bridging oxygen is also observed after poling in more than 80 oxide glasses including aluminosilicates and borosilicates. Overall, our study shows that MD can be a highly effective tool to gain valuable insights into the significant structural rearrangements that occur in glass networks during thermal poling.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In thermal poling, a DC voltage on the order of a few hundreds to thousands of Volts is applied to a glass sample at moderate temperature (usually <500 °C) [1]. The presence of this external electric field promotes spatial rearrangement of charged mobile species within the glass network [2]. The displacement of alkali and alkaline earth atoms towards the cathode creates a network former-rich depletion layer in the sub-anodic region, as represented in Fig. 1. As a result, an anisotropic redistribution of charges within the glass sample takes place [1,2,3]. Such compositional and structural modifications have been linked to changes in refractive index as well as second-order nonlinear (SONL) optical response due to the creation of a static electric field within the glass [4,5,6,7]. These effects are key factors explaining the extensive use of thermal poling for applications in photonic devices.

Over the years, many studies have investigated potential industrial applications for this technique as well as the extent of compositional and structural changes induced by thermal poling on different glasses [8–11]. The nature of the electrodes used has been found to significantly influence the nature of the depletion layer [12,13]. If open electrodes are used, the entire process becomes a field-assisted ion exchange where external cations usually from the atmosphere (e.g., H₃O⁺) or from ionization of a metallic electrode, are added to the glass network in

replacement of the departed network modifiers [12,14–16]. Alternatively, if blocking electrodes are used, negatively charged carriers leave the glass network. This is exemplified in oxide glasses by a recombination of oxygen ions into molecular oxygen [17,18].

In order to put the compositional and structural changes created by thermal poling in context, a quick overview of the general process by which glass networks are formed will be useful. In general, silicate glasses are considered to form a network of connected SiO₄ tetrahedra that share oxygen atoms called “bridging oxygen” [19]. The addition of alumina or boron oxide increases the connectivity of the network by creating additional corner-shared polyhedra in the network. When other species such as sodium oxide or calcium oxide are introduced, these new cations will break previous bonds and create non-bridging oxygen atoms [20]. Alternatively, they can help charge-compensate over-coordinated aluminum atoms or convert boron atoms from 3-coordination to 4-coordination [21,22].

Despite all the progress made over the years, a good understanding of the full extent by which a glass network gets altered by thermal poling as well as the mechanism of such changes are still being investigated by multiple researchers [15–18,23]. A unifying theory that can explain the effect of thermal poling on mechanical, physical and chemical properties of any glass composition based on processing parameters such as temperature and applied voltage is still missing. Among other questions, the nature and influence of the interface region between the depletion and non-poled layers are not fully understood. Moreover, with the early focus on optical properties, only a few reports have

* Corresponding author.

E-mail address: tandia@corning.com (A. Tandia).

investigated the effects of thermal poling on other properties such as elastic properties.

If a unifying theory predicting poling-induced property changes for a wide range of glass compositions is to be developed, the use of computational techniques in addition to experiments could offer significant advantages. For instance, the number of different glass compositions that can be studied in a given amount of time will be greatly extended. Also, molecular resolution into the structure can be achieved as individual atoms are modeled explicitly. For this study, we use MD to simulate more than 80 different oxide glasses including aluminosilicates and borosilicates with four different network modifiers: sodium, lithium, calcium and magnesium. We compute structural properties such as Al and B coordination numbers as well as population of bridging and non-bridging oxygen before and after poling and compare them with experimental results. To the best of our knowledge, this is the first comprehensive study showing that MD can successfully reproduce experimentally observed structural changes in oxide glasses caused by thermal poling. Such a study creates the necessary stepping stone for subsequent in-depth computational studies of the effects of thermal poling on other properties of oxide glasses.

2. Methods

2.1. Glass compositions

In order to gain much broader insights into the structural effects of thermal poling on oxide glasses, we simulated aluminosilicates and borosilicates with concentrations of network modifiers of up to 25% mole percent. These calculations were repeated for four different network modifiers: Li_2O , Na_2O , CaO , and MgO . The glass compositions simulated as part of this study are listed in Table 1 where “X” corresponds to boron or aluminum, “R” to sodium or lithium, and “M” to calcium or magnesium totalizing over 80 different glasses. The ratio of $\text{SiO}_2/\text{X}_2\text{O}_3$ was kept constant for all the glasses studied in this work.

2.2. As-melted and poled glass structure generation

In order to generate the as-melted glass structures, Packmol [24] was used to pack a total of roughly 20,000 atoms in a cubic box of dimensions corresponding to an initial arbitrary density of 2.80 g/cm^3 . Isothermal isobaric (NPT) MD simulations were then performed allowing the box to relax to its optimal dimensions under zero stress. In order to provide enough thermal energy for the different atoms to attain equilibrium-like positions, the temperature was ramped from 300 K to 4000 K and then slowly quenched back to 300 K within 8 ns. The Pedone [25] force field, which is widely used in the glass modeling community, was also used in this work. The choice of this force field was also motivated by the fact that it was developed for, and shown to offer good predictions of, both structural and mechanical properties of oxide glasses [26–28]. Moreover, those parameters were developed to ensure proper values for elastic properties, which will be the subject of part II of this study [25]. The electrostatic interactions are handled with the particle-particle particle-mesh (PPPM) Ewald method [29,30].

Since the focus of this work was to investigate the structural effects of thermal poling from a thermodynamics perspective rather than understanding the kinetics of the process, the poled structures were

obtained by removing all the network modifiers and associated oxygen atoms at once after the initial structures were equilibrated. Direct removal or substitution of atoms has been successfully used before to study effects of ion exchange on network lattice dilation and elastic property variation in glasses [27,28]. Also, it is worth noting that the simulated poled structure corresponds to what is found inside the poled layer near the surface, but sufficiently away from the intermediate region characterized by increasing concentration of network modifiers (see Fig. 1).

NPT simulations at 300 K under zero stress were then performed to obtain the equilibrium structures after poling. LAMMPS [31] and Gromacs [32–34] were used for the MD simulations. LAMMPS was used because of its superior scripting interface, which allows for more flexibility to implement custom energy minimization and simulation processes for poled and as-melted glass structure generation. Gromacs was used to perform specific MD runs because of its speed advantage due to the large number of simulations performed in this project. We used the same force field parameters in LAMMPS and Gromacs. We also used an additional criterion for convergence based on the density uniformity within 1% of fluctuation throughout the glass structures. The local densities were measured by iteratively dividing the simulation box into smaller boxes ensuring a more thorough structure validation.

2.3. Coordination number analysis

A thorough coordination number analysis was performed for both poled and as-melted structures obtained after careful equilibration. We compute coordination number from the integration of the radial distribution function up to the first minimum after the first peak. Statistics collected included the percentage of each atom found in a given coordination state as well as a breakdown of the atom to which they are connected. In that way, a deep understanding of the short-range local environment of each atom is obtained for both the poled and as-melted glass networks. Special attention is given to the fraction of bridging and non-bridging oxygen in as-melted, poled and pure structures. These metrics are chosen because they are routinely used by experimentalists to characterize glass networks [35–38] and, therefore, offer the opportunity for direct comparison between our results and experimental observations. Although we did not focus on the kinetics of thermal poling, some data were also collected related to how the Pedone force field handles the rearrangement of the glass structure. These data are used to lend more insights into the advantages and limitations of using MD to model thermal poling (Fig. 1).

3. Results

3.1. Conversion of B^{IV} to B^{III}

Fig. 2 shows the fraction of three- and four-coordinated boron as a function of mole percent of network modifiers before and after poling. As expected in the as-melted compositions, the concentration of B^{IV} increases with mole percent of network modifiers, while the concentration of B^{III} decreases. The tendency of boron to adopt a four-coordinated state in the presence of network modifiers in silicate glasses has been extensively documented in prior literature [23,39]. For all four network modifiers, after thermal poling, we observe a clear conversion of all the B^{IV} created with the addition of alkali and alkaline earth to a corresponding fraction of B^{III} . This conversion could be explained in part by the absence of network modifiers providing charge compensation to the B^{IV} units. These $[\text{BO}_4]^-$ are therefore converted to $[\text{BO}_3]$, which are charge-neutral and therefore do not need charge compensation. This conversion from tetrahedral B^{IV} to trigonal B^{III} has been documented before in experiments [23,40,41]. Nonetheless, it is worth noting the difference in fractions of B^{IV} in as-melted glass structures for different types of network modifiers. Our findings for Ca generating more B^{IV} than Mg is consistent with previous experimental studies on

Table 1
Glass compositions simulated as part of this study.

SiO_2 (mol%)	X_2O_3 (mol%)	$\text{R}_2\text{O/MO}$ (mol%)
66.28	33.72	0.00
64.98	33.06	1.96
61.94	31.51	6.54
58.65	29.84	11.50
54.78	27.87	17.36
50.21	25.55	24.24

Download English Version:

<https://daneshyari.com/en/article/5441366>

Download Persian Version:

<https://daneshyari.com/article/5441366>

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