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Modeling the thermal poling of glasses using molecular dynamics. Part 2: Effects on elastic properties

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ABSTRACT

In this work, thermal poling of ternary oxide glasses, including borosilicates and aluminosilicates, is studied using molecular dynamics. For the glass compositions simulated, results show that thermal poling lowers the Young's modulus of those ternary oxide glasses. Additionally, comparisons between the structures of as-melted and poled glasses, as well as comparisons with their binary as-melted counterparts of the same composition, reveal that the changes in elastic properties can be partially attributed to changes in void size distributions within those glass networks. Overall, this study shows that thermal poling can effectively be used to alter the elastic properties of oxide glasses.

1. Introduction

Post-processing techniques capable of modifying surface properties of glasses after melting are desirable for many applications. For instance, using appropriate techniques, glass surfaces can be modified for optimal binding with application-specific coating materials or designed for enhanced scratch resistance. Thermal poling is one such technique that is already in use for several purposes, including for its second-order nonlinear (SONL) optical effects on glasses [1,2,3] and for its ability to modify structural properties of nanoparticle embedded glasses for large-scale complex plasmonic nanostructures fabrication [4,5,6,7,8]. In this work, we investigate how thermal poling can be used to alter mechanical properties of glass surfaces.

In general, thermal poling refers to the use of an electric field to promote the creation of a network-modifier depleted layer near the anode, as shown in Fig. 1. One of the first published reports on the use of such a technique is usually attributed to Carlson *et al.* in a 1972 article on polarization in alkali-containing glasses [9]. Since the earliest applications of this technique aimed to take advantage of the induced polarization created after poling, many studies focused on understanding the origins of this effect as well as the influence of process variables such as the nature of electrodes, voltage, and temperature [10,11,12]. Preliminary studies have also been done to understand the kinetics of thermal poling and the elementary reactions that take place to allow for such extensive rearrangement of the glass network [13,14,15,16].

In this study, we use molecular dynamics (MD) to investigate the effects of thermal poling on the elastic properties of oxide glasses. The goal of this work is to understand the differences in elastic properties within the poled layer compared to the bulk as-melted glass. The scope is intentionally limited to the thermodynamics, rather than kinetics, of the thermal poling process. In other words, we do not model, nor do we attempt to elucidate, the mechanisms by which thermal poling takes place. This restriction in scope is justified by the fact that outstanding questions remain regarding the underlying mechanisms by which thermal poling takes place. For instance, what are the preferred poling-induced migration paths of network modifiers? When blocking electrodes are used, what are the reactions leading to molecular oxygen formation? Etc. Those questions are still not fully answered and require separate kinetic studies to answer them.

In order to obtain a more general idea of the extent of changes in elastic properties due to thermal poling, ternary borosilicates and aluminosilicates were studied with different mole percent concentrations of one of four different network modifiers. We consider two types of alkali oxides (Li_2O and Na_2O) and two types of alkaline earth oxides (MgO and CaO). The compositions studied in this work are shown in Fig. 2. After poling of the ternary glasses, their final composition corresponds to a pure binary with 66.28 mol% SiO_2 and 33.72 mol% X_2O_3 where X = {B, Al}.

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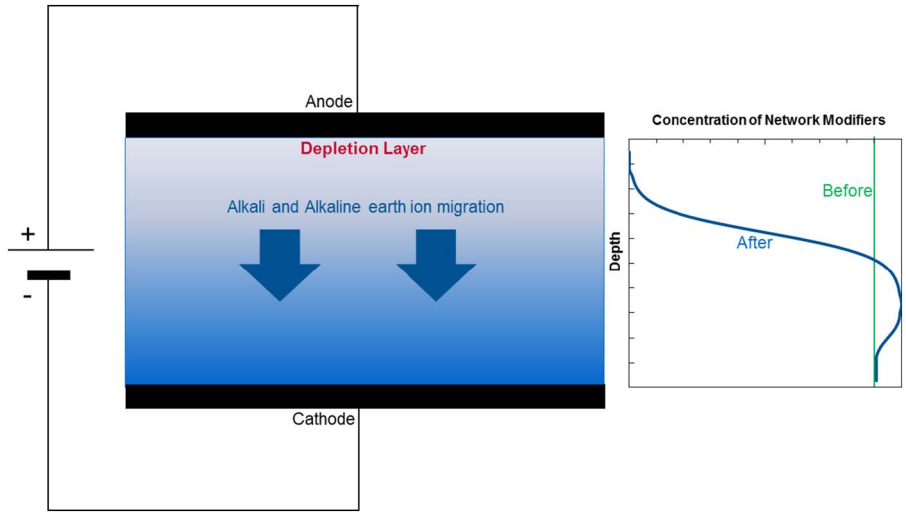

Fig. 1. Schematic representation of a thermal poling setup. The process of thermal poling leads to a depletion layer in the sub-anodic region due the migration of cations towards the cathode. Typical length scale of the depletion layer is on the order of hundreds of nanometers to up to several micrometers. This work focuses on understanding changes in elastic properties in the depletion layer.

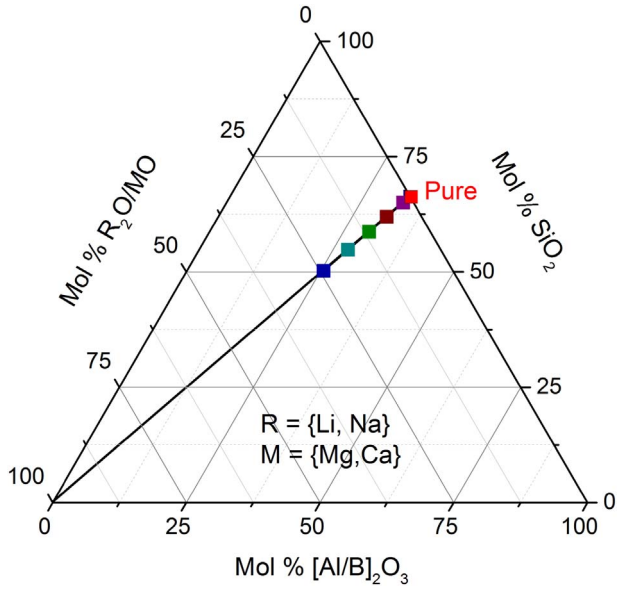

Fig. 2. Ternary glass compositions considered in this work. Thermal poling of a ternary glass creates a layer depleted of network modifiers, leading to a binary glass composition. All the glasses studied in this work lead to the same composition of the final binary glass labeled as “Pure”.

2. Methods

2.1. Glass structure generation

We use the force field developed by Pedone et al. [17] optimized for mechanical properties of oxide glasses. Atoms were packed in a cubic box of dimensions corresponding to an initial arbitrary density of roughly 2.8 g/cm^3. Isothermal-isobaric NPT Molecular Dynamics simulations were then carried out allowing the box to relax to its zero-pressure state. Similar to previous studies, the temperature was slowly ramped up to 4000 K over 2 ns, then back down to 300 K over 8 ns [18,19]. Packmol [20] was used to randomly pack atoms in simulation boxes.

LAMMPS [21] and Gromacs [22,23,24] 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. The same force field parameters were used in LAMMPS and Gromacs. An additional criterion based on density uniformity within 1% of fluctuation throughout the glass structures was also used for convergence. The local densities were measured by iteratively dividing the simulation box into smaller boxes ensuring a more thorough structure validation.

Although outside the depletion layer, the concentration of network modifiers is expected to be non-uniform, the limited scope of this study (which excludes kinetic effects) as well as the fact that we focus only on the structure inside the depletion layer (characterized by the absence of network modifiers), render the isotropic assumption in our simulations reasonable. Moreover, we do not believe the network modifiers' migration pathways would permanently alter the glass network within the depletion layer in an anisotropic fashion. The moderate sub-glass transition temperature would not allow for a significant distortion of the remaining network formers as the migration of the network modifiers is primarily through diffusion to which the electric field provides a bias.

Consequently, and since only the thermodynamic effects are of interest, the poled structures were obtained by brute-force removal of cations and oxygen from previously equilibrated glasses. The oxygen atoms to remove are the ones that fall within the first minimum of the radial distribution function between oxygen and the cation of interest. The resulting structure was subjected to subsequent NPT equilibrations until density fluctuations reached a minimum. NPT simulations were used instead of NVT because thermal poling experiments usually take place in atmospheric pressure and therefore, the volume of the glasses is not constrained. Using glass compositions similar to the ones used in this study, Tandia et al. [25] previously validated this method (brute force removal of network modifiers followed by NPT simulations) in terms of its effectiveness to properly reproduce structural characteristics such as changes in coordination number and non-bridging oxygen elimination in poled glasses.

2.2. Elastic property calculation

The generalized Hooke's law relating the stress (σ) and strain (ϵ) tensor for an isotropic system is given by Eq. 1, where E is Young's modulus and ν Poisson's ratio. ϵ_{ii} denotes the diagonal element of the strain tensor, σ_{ii} is the corresponding stress element.