



Hole traps in sodium silicate: First-principles calculations of the mobility edge



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ABSTRACT

The structure and properties of $(\text{Na}_2\text{O})_{0.30}(\text{SiO}_2)_{0.70}$ sodium silicate glass are studied by combined ab-initio and classical molecular dynamics simulations to identify the sources of electronic traps in the band gap. Structures from classical molecular dynamics melt-quench simulations are taken as initial configurations for first-principles density functional theory structural relaxation, from which electronic properties are determined. An ensemble of thirty glass structures, each containing 660 atoms, is prepared in order to perform statistical analyses. The inverse participation ratio is used as a metric to characterize localized states in the band gap and determine the mobility edge. Structures with varying amounts of local disorder (traps) are compared. The most localized and highest energy trap states are due to Si atoms with 2–3 non-bridging oxygen atoms. Control of the electronic properties of amorphous insulators and semiconductors is essential for the advancement of many technologies, such as photovoltaics and scintillators, for which the present analysis is indispensable.

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1. Introduction

The ability to improve or control the electronic conductivity of amorphous insulators will lead to significant advances in many technologies, such as scintillating materials, electrochemical cells, and photovoltaics. First-principles calculations of crystalline electronic structures have enabled the technological development of many materials, such as silicon [1], but similar advances in glasses and amorphous materials have been frustrated by the significantly larger computational demands of simulating amorphous materials.

The properties of both amorphous and crystalline materials can be controlled by engineering their local structure and defects. Electronic conductivity is sensitive to substitutional atoms or vacancies that leave dangling bonds, which can donate electronic carriers or trap them. The electronic structure calculations presented in this paper relate the local structure of dangling bonds in sodium silicate glass to electronic traps in and near the band gap. Using first-principles methods to simulate amorphous materials requires judicious selection of an adequately large cell size and simulation length; state of the art supercomputers are making this task possible [2,3]. Running simulations in parallel on supercomputers also allows statistics to be gathered from an ensemble of structures, as is done for sodium silicate in this study.

Low electronic conductivities in amorphous insulators are not only due to large effective masses, as in wide gap crystalline insulators, but also to carrier traps [4]. We calculate the mobility edge and nature of

charge traps in a prototypical amorphous material sodium silicate, which is representative of the alkali-silicates. Alkali and alkali-earth cations are silica network modifiers that create non-bridging oxygen atoms (NBOs) and serve a wide variety of technological applications, such as reducing crystallization [5] and decreasing the glass-transition temperature and water solubility [6]. Compared to silica, which has fewer NBOs, these dangling bonds affect the mobility gap and edge, which distinguishes between delocalized versus localized electronic bands that accommodate band like conductivity versus trap charge, respectively. Ce-doped silica is a candidate material for scintillators, but the low mobility of electrons and holes and the low solubility of Ce-dopants means the charge carriers do not often diffuse to the Ce-activator dopants, which has limited its technological use [7].

Theoretical models of electronic conductivity in amorphous insulators started with the seminal paper by Mott in 1977 [8]. By 1980, Mott's theories of electron traps and hopping (as contrasted with band-like conductivity) had been applied to explain optical phenomena in sodium silicate [9]. However, the electronic conductivity is difficult to measure conventionally, especially in the case of alkali-silicates, where ionic conduction by the alkali ion can be significant. Luckily, measurements of the luminescence or scintillation of a material can selectively probe the conductivity of electrons and holes. For example, researchers developing scintillating glasses have observed no scintillation in Ce-doped sodium trisilicate compared to Ce-doped silica [10,11,7], giving indirect evidence of significantly poorer carrier transport in the sodium silicate host. Radio-scintillation efficiency is a measure of carrier transport, because photogenerated electrons and holes must migrate to the activator dopant Ce atoms for scintillation to occur [12]. However, the microscopic cause of the degraded energy transfer in sodium silicate versus silica remains undetermined,

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especially since there have been very few first-principles studies of electronic transport in alkali glasses.

A detailed analysis of the electronic structure of sodium silicate from first-principles can reveal the structure–property relationship between defects and electronic mobility. Though the electronic structure of silica is well-established [13,14], there have been only a few, small (90 atoms [15] and 120 atoms [16]) first-principles studies that compare the effect of the NBOs and other atomic-scale defects on the electronic structure of sodium silicate. In Ref. [15], the electronic density of states (DOS) from two $(\text{Na}_2\text{O})_{0.20}(\text{SiO}_2)_{0.80}$ configurations were compared with the DOS from silica, but in a way that obscures the trap states that form in the gap. Our analysis of $(\text{Na}_2\text{O})_{0.30}(\text{SiO}_2)_{0.70}$, which contains a higher concentration of NBOs than in Ref. [15], identifies the atomic geometries of the NBOs in the mobility gap. Our simulation cell was chosen to be large (660 atoms) so that an ensemble of structures would achieve a good statistical representation of the structure in macroscopic volumes.

2. Simulation details

Simulations of the structure of amorphous materials often employ classical potentials to allow the sampling of many statistically independent configurations. In contrast, first-principles (density functional theory-based) molecular dynamics simulations of structures with hundreds of atoms are often limited to only 10's of picoseconds in length, which is too short to collect uncorrelated time samples. Reverse Monte Carlo techniques have also been employed to simulate amorphous structures [17], but the effect of the glass forming procedure cannot be studied with this method. Thus, we use a classical potential to create glass structures by quenching the melt at quench rates between 10^{11} K/s and 10^{14} K/s. We simulate the 30:70 $\text{Na}_2\text{O}:\text{SiO}_2$ glass (30:70NS) and compare it with lower Na content tetrasilicate glass (20:80NS). The prior study on 20:80NS used a variable charge BKS two-body potential and quenched from 3500 K to 300 K at a rate of 5×10^{13} K/s. We use a three-body potential based on a modified Born–Mayer–Huggins (BMH) ionic potential, described in Ref. [18], with recently optimized parameters,² which we implemented in the lammmps MD code [19].

The glass forming procedure starts with swapping out Si and O atoms for Na from a $4 \times 4 \times 4$ β -cristobalite cell and setting the volume to correspond to the experimental density of 2.466 g/cm³. Our 30:70NS simulation cells have 154 SiO_2 formula units and 66 Na_2O formula units. A time step of 1 fs was employed using the Langevin thermostat with a 1.0 ps damping parameter to control temperature.

Initial structures are generated using the classical potential and the following steps. First, the forces on the atoms are minimized and then the temperature is increased from 300 to 8000 K over 6000 ps, as the volume is scaled up 116% to take into account thermal expansion. The melt is held at 8000 K for 80 ps, after which 30 snapshots are taken every 32,000 steps (32 ps), in order to create an ensemble of independent glass structures. The melt structure from each snapshot is quenched back down to 300 K over 80,000 steps (80 ps), while rescaling the volume every 8000 steps. This corresponds to a quench rate of 9.6×10^{13} K/s, although quench rates as slow as 10^{11} K/s were tested and compared. We find a glass transition temperature around 3000 K. The 30:70NS structures compare well to other simulations from the literature, as will be described in the Results section. Finally, each snapshot is equilibrated at 300 K for 80 ps from which structural statistics are collected.

The final room temperature structures from the above procedure using classical MD are not immediately used to calculate the electronic structure, because very large residual forces remain on the atoms. Thus, each structure is further relaxed with density functional theory (DFT) using the PBE exchange–correlation functional [20,21] to reduce

the forces on all atoms to less than 0.05 eV/Å. A planewave cutoff of 700 eV is used to ensure accuracy, based on tests of SiO_2 , with only the Γ -point used to sample the Brillouin zone. The VASP code [22–25] and the projector-augmented wave method [26,27] was used for all DFT calculations.

The localization of each electronic state near the band gap is quantified using the inverse participation ratio (IPR), which is related to the second moment of the charge density. The IPR compares the spatial extent of a given wave function, ψ_n , to the total probability density, on a scale from 1 to N , where 1 is delocalized and N is very localized. Specifically, the IPR is calculated from the band-decomposed partial charge density, $|\psi_n(\vec{r}_i)|^2$, via

$$I(\psi_n) = N \frac{\sum_{i=1}^N |\psi_n(\vec{r}_i)|^4}{\left[\sum_{i=1}^N |\psi_n(\vec{r}_i)|^2 \right]^2}, \quad (1)$$

where i labels the real-space grid points upon which the charge density is computed, N is the total number of grid points (and maximum IPR value), and n is the band index. For the calculations of IPR, the plane wave cut-off was reduced to 400 eV without loss of accuracy.

All computed quantities are averaged over the ensemble of 30 configurations to capture the wide structural variations and range of defects of a bulk glass sample.

3. Results

3.1. Glass structure

The structural analysis of our glass model highlights how the addition of sodium breaks up the network structure of silica.

The metrics we calculate also indicate the quality of the simulation procedure and the potentials used. While, in principle, the most reliable structures would be obtained from performing the melt-quench simulations entirely using DFT, computational feasibility dictates that initial structures be generated using melt-quench MD simulations with classical potentials and then relaxed post-quench with DFT. While the DFT relaxation does change the local structure slightly, the classical potential predominantly determines the structural statistics of the generated glass models.

The addition of sodium to silica disrupts the Si—O—Si bonds, and should generate approximately one non-bridging oxygen atom (NBO) per Na atom, in a Si—O—Na configuration. In our simulations of 30:70NS, there are $34 \pm 0.0\%$ NBO, which is close to the sodium concentration. In Ispas et al.'s calculation of 20:80NS, a NBO concentration of 22% was found, which is also similar to, but slightly higher than, the concentration of Na in the system. The non-bridging oxygen atoms are the primary source of trap states in the mobility gap and near the valence band maximum (i.e., Urbach tails) [28,29], and this is discussed in more detail below.

Each Si cation can bond to 0–4 NBO atoms, with increasing NBO being less energetically favorable. The number of bridging oxygen (BO) atoms bonded to a given Si atom defines its Q^n value, such that a Si atom with $n = 4$ BO atoms is defined as a Q^4 Si, whereas a Si atom with $n = 1$ BO atom is defined as a Q^1 Si [30]. Each NBO is labeled by the Q^n value of the Si to which it is bonded. A subscript will be added to the label to indicate the oxygen and if there are no NBO, these oxygen will be labeled Q^4_δ .

In addition, each localized NBO can be assigned an energy level by associating it with a band in the electronic structure, using the following steps:

- (i) first, the band structure is calculated and NBO's Q^0_δ values are assigned;

² S.H. Garofalini, private communication.

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