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# Effects of Magnesium on the Structure of Aluminoborosilicate Glasses: NMR Assessment of Interatomic Potentials Models for Molecular Dynamics

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## Abstract

Classical Molecular Dynamics has been used to investigate the structural impact of Mg incorporation in a series of sodium aluminoborosilicate glasses. The simulations have been performed using three forms of interatomic potentials. The first is based on a standard rigid ionic model (RI) as parameterized by Wang et al. (1) and used in a previous work on the same glass compositions (2). The two others potentials implement the core-shell model (SM) (to account for the polarization of oxygen atoms) provided by Stevensson et al. (3) (SM1) and Pedone et al. (4) (SM2). The two SM models differs in the B-O interactions parameters. SM2 was refined from SM1 to better simulate glasses with high BO<sub>4</sub> content by Pedone et al.(4). The accuracy of these models have been assessed by both a detailed structural analysis and a thorough comparison of the simulated NMR spectra for the spin active nuclei <sup>29</sup>Si, <sup>27</sup>Al, <sup>11</sup>B, <sup>17</sup>O, <sup>25</sup>Mg, and <sup>23</sup>Na with the experimental counterparts collected in a previous work (5).

Our simulations reveals that the SM parameterizations provide much better structural models. Notably, they better reproduce the NMR spectra of all the investigated nuclei and give better agreement with known experimental data. For example, SM1 predicts the N<sub>4</sub> fraction in the glass series accurately whereas RI gives a large overestimation. Furthermore, RI always gives a non-negligible amount of Al in high coordination state (AlO<sub>5</sub>) while SM potentials predict very low values. In addition, if the RI force field predicts a non-negligible amount of Al-NBO linkages and the highest B<sub>4</sub>-NBO bonds, the core-shell potentials do not predict NBO on Al and minor percentages of NBO in B<sub>4</sub>, especially with the SM2 modified parameters.

All the NMR spectra simulated with SM1 and SM2 gives a much better agreement with experiments, thus validating the simulated structures. In particular, <sup>17</sup>O MQMAS NMR spectra is better reproduced by SM2 force field, while <sup>11</sup>B MAS NMR spectra by the original SM1 one.

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Concerning the structural role of Magnesium, the latter is found to be five coordinated on average with Mg-O distances in between a network modifier (like Na) and an intermediate network formed (like Al). Our MD simulations shows that Mg prefers to lay closer to 3-coordinated boron atoms, forming BO<sub>3</sub>-NBO bonds, with respect to silicon and especially aluminum atoms. This can explain the formation of AlO<sub>5</sub> and AlO<sub>6</sub> units in the investigated Na-free glass, together with a silicon network clusterization as suggested by 17O MQMAS NMR data.

(1) M. Wang et al., *A New Transferable Interatomic Potential for Molecular Dynamics Simulations of Borosilicate Glasses* J. Non-Cryst. Sol **2018**, 498, 294-304.

(2) N. Bisbrouck et al., *Influence of Magnesium on the Structure of Complex Multicomponent Silicates: Insights from Molecular Simulations and Neutron Scattering Experiments*, J. Phys. Chem. B **2021**, 125, 11761–11776.

(3) B. Stevansson et al., *Structure–Composition Trends in Multicomponent Borosilicate-Based Glasses Deduced from Molecular Dynamics Simulations with Improved B–O and P–O Force Fields*, Phys. Chem. Chem. Phys. **2018**, 20 , 8192–8209.

(4) N. Stone-Weiss et al., *Combined Experimental and Computational Approach toward the Structural Design of Borosilicate-Based Bioactive Glasses*, J. Phys. Chem. C **2020**, 124, 17655–17674

(5) N. Bisbrouck et al., *Impact of Magnesium on the Structure of Aluminoborosilicate Glasses: A Solid-State NMR and Raman Spectroscopy Study*, Journal of the American Ceramic Society **2021**, 104, 4518–4536

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