

論文名 : Structural Study of Aluminosilicate Glasses by Developing Polarizable Force Fields (要約)

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Aluminosilicate glasses are made of tetrahedral SiO_4 and AlO_4 units due to the coexistence of alkali and alkaline-earth ions, that is, network modifiers. Since polymerization of the structural units improves the chemical durability and mechanical strength, and they can be further improved through the ion-exchanging procedure on the glass surface such as Corning® Gorilla® Glass,[1] one of the significant challenges is to elucidate the relationship between structures and physical properties in aluminosilicate glasses. In this study, in order to investigate the properties of network former and modifier accurately, polarizable force-fields were developed on the basis of first-principles calculation with density functional theory (DFT). The coordination and network structures of aluminosilicate glasses were evaluated by using molecular dynamics (MD) calculation with obtained force fields. They were compared with corresponding experimental data and first-principles calculations to confirm the validity of polarizable force-fields. The roles of network former cations and bridging oxygens, and the effects of network modifiers in network structures were investigated over the wide ranges of compositions.

Topics of Chapter 1 are scientific and industrial interests of aluminosilicate glasses, the history and present status of studies with experimental and computational approaches, and the significance and purpose of this study. Topics of Chapter 2 are the description of functional forms, potential parameters, and the method of fitting procedure in the present force fields: polarizable ion model (PIM) and aspherical ion model (AIM). The other detail conditions of MD calculation are also described in this chapter.

In Section 1 of Chapter 3, the accuracy of PIM and AIM force-fields is described with the reference data of first-principles calculation in NaAlSiO_4 melt and the glass. In Section 2 of Chapter 3, the structures and stability in crystalline polymorphs are compared between structural models obtained with PIM and AIM. Their results prove that including the anisotropic repulsive interaction of oxygen ions (considered only in AIM) improves the agreement with first-principles calculation, and provides more realistic structures for network former cations and bridging oxygens. Thereby, it is concluded that the deformation effects of oxygen ions should be taken into consideration for accurate structural modelling of aluminosilicates by MD calculation.

In Section 3 of Chapter 3, the structure factor, radial distribution function, bond length, coordination number, bond angle distribution of structural units obtained with AIM are described over the wide range of compositions of sodium aluminosilicate glasses. The fraction of bridging

oxygen species and the ^{17}O MQMAS NMR spectrum are also discussed in Section 4 of Chapter 3. Almost all the obtained results show excellent agreements with the corresponding experimental values. Although the $\sim 5\%$ of five-coordinated Al^{3+} is observed even in the charge compensated compositions, it has been experimentally detected in the peralkaline and charge compensated compositions of sodium and calcium aluminosilicate glasses, respectively. Therefore, it is concluded that structural models obtained with AIM are very realistic on the level of ^{17}O MQMAS NMR spectrum.

Here, it is noted that the AIM force-field shows high transferability over the wide ranges of thermodynamic conditions and compositions, in comparison with classical empirical force-fields provided in previous studies.[2] The computation cost also remains relatively lower in the framework of polarizable force-fields, since the functional form was optimized to effectively express the interionic interactions of DFT calculation. Therefore, the present force-field enables to perform large-scale and long-time MD calculations of aluminosilicates with high accuracy.

In Section 5 of Chapter 3, the effects of network modifier on the structure of bridging oxygens (BOs) are described in sodium aluminosilicate glasses. In the Section 6, they are extended to the general network modifiers: Li^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+} . The relationship between structures and mechanical properties are also discussed in the Section 7. In sodium aluminosilicate glasses, while the bridging angle distribution of Si-BO-Si and Si-BO-Al shows a sharp peak regardless of compositions, the bridging angle of Al-BO-Al is quite deformable and dependent on the fraction of network modifier. Here it is noted that the experimental Young's modulus, correlating with hardness and fracture toughness, remains independent on the fractions of BO species. These results may imply that there is no difference for the effects on mechanical properties between BO species. In aluminosilicate glasses of different network modifiers, the bridging angle of Al-BO-Al is very sensitive to network modifier species. Furthermore, the increase of number density of network backbone decreases the fractions of Al-O-Al and Si-O-Al, and increases the fractions of five-coordinated Al^{3+} and three-bridging oxygen. Therefore, it is found that the volume contraction due to the presence of network modifiers deforms the bridging oxygen of Al-BO-Al, and as a result, generates five-coordinated Al^{3+} ions and three-bridging oxygens.

[1] L. Wondraczek, J. C. Mauro, J. Eckert, U. Kühn, J. Horbach, J. Deubener, T. Rouxel, *Adv. Mater.* **23**, 4578 (2011).

[2] M. Carlo, D. Jincheng, B. Marco and S. S. Philip, *Molecular Dynamics Simulations of Disordered Materials*, 1st ed. (Springer International Publishing, Switzerland, 2015).