

Atomic and electronic structures of binary silicate glasses

Glass is abundant in nature and has been made by man for over 3000 years. Glass has evolved from a basic structural material to an enabling material for advanced electronic, biological and photonic products as well as high-volume window and fiber glass devices. Despite its rich history, many aspects of glass remain mysterious: The theory of glass transition is one of the most challenging problems in physics and chemistry in the 21st century.

The PbO-SiO₂ system is interesting even though lead compounds are unfavorable materials nowadays. It is well known that PbO acts both as a glass former and a glass modifier and hence the PbO-SiO₂ system shows a wide glass formation composition range. Therefore, it is interesting to know the underlying reason through the atomic structure of glass. Atomic structures of magnesium silicate melts are the key to understanding the processes related to the evolution of the Earth's mantle and represent precursors of the formation of most igneous rocks. Magnesium silicate compositions also represent a major component of many glass ceramics, and, depending on their composition, can span the entire fragility range of glass formation. It is worth mentioning that glass of Mg₂SiO₄ composition shows an extremely low glass forming ability (GFA), while MgSiO₃ composition shows a higher GFA. Therefore, we have tried to understand the relationship between glass structure

and GFA at atomic and electronic levels by a combination of high-energy X-ray diffraction (BL04B2) and neutron diffraction measurements, reverse Monte Carlo (RMC) simulations, and density functional theory (DFT) calculations [1,2].

Figure 1 shows the cavity distribution in SiO₂ and PbO-SiO₂ glasses obtained by RMC simulation. It is well known that SiO₂ glass shows a large fraction of cavities (~30%), but we can see a significant amount of cavities in PbO-SiO₂. This is very unusual, since cavity sites are usually occupied by cations in typical binary silicate glasses (e.g., Na₂O-SiO₂ and CaO-SiO₂ glasses). Lead is known to act as a network former and a network modifier in binary oxide glasses. Thus, we have succeeded in visualizing the role of lead in PbO-SiO₂ glass, suggesting that the large fraction of cavities is the reason for the high GFA in a wide composition range.

On the other hand, both MgSiO₃ and Mg₂SiO₄ glasses do not have any cavities, because magnesium occupies cavity sites in binary silicate glasses. To understand the relationship between GFA and atomic structure, we compared the distribution of “-Si(Mg)-O-Si(Mg)-O-Si(Mg)-” rings in MgSiO₃ and Mg₂SiO₄ glasses with the distribution of “-Si-O-Si-O-Si-” rings in SiO₂ glass in Fig. 2. The ring distribution of SiO₂ glass shows the maximum fraction of 6-fold rings (comprising 6 SiO₄ tetrahedra) and is broad up to

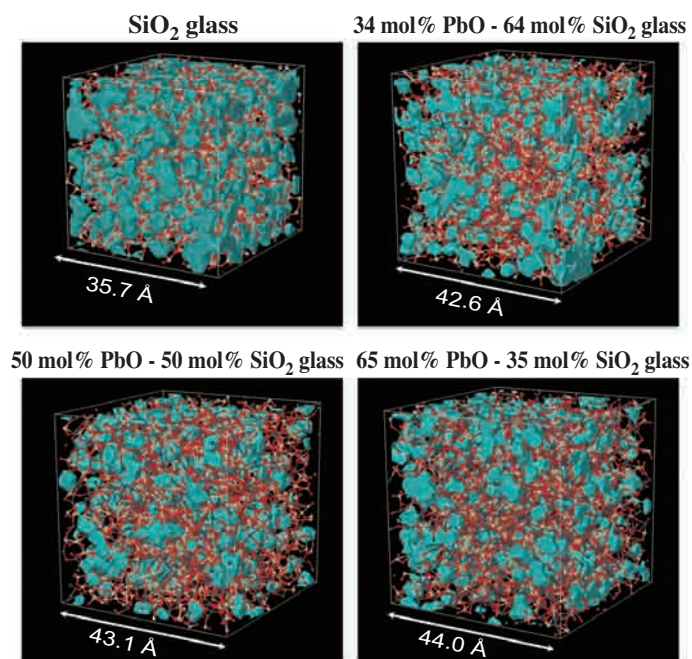


Fig. 1. Atomic configurations and voids of SiO₂ and PbO-SiO₂ glasses. Color key: light gray, silicon; red, oxygen; gray, lead; and cyan, voids [1].

10-fold rings. According to Gupta and Cooper, this distribution is the signature of “topological disorder”, since the crystalline SiO_2 (cristobalite) has only 6-fold rings [3]. On the other hand, Mg_2SiO_4 glass shows the narrowest ring distribution, suggesting that it is “topologically ordered”, which is related to the low GFA of the glass.

The coordination numbers of oxygen around magnesium derived from the RMC model are 4 and 5 for MgSiO_3 and Mg_2SiO_4 , respectively, which do not support the formation of MgO_6 octahedra confirmed by recent NMR measurements for both glasses [4,5]. To obtain insight regarding this inconsistency, we optimized the RMC structures by DFT calculations. Furthermore, we calculated chemical strength (bond orders) for Mg-O bonds in both MgSiO_3 and Mg_2SiO_4 crystals and glasses. The Mg-O bond orders of glasses shown in Fig. 3 are larger than those of the corresponding crystalline phases owing to the fact that the Mg-O coordination is smaller in the glassy phase, where the cations compensate the smaller number of oxygen contacts by increasing the ionic bond strength correspondingly. The DFT calculations explain the discrepancy between the NMR and diffraction results, because NMR probes chemical shifts that are very sensitive to the electronic environment of the nuclei, while diffraction is a direct probe of the average coordination number through known neutron scattering lengths or the number of electrons surrounding an atom (provided that the partial functions are known). Previous studies [4,5] indicated that for the MgSiO_3 and Mg_2SiO_4 glasses, the NMR shifts are in line with the octahedral crystalline environment, although in this study we find that the Mg-O coordination is actually smaller in the glasses.

The structure of disordered materials is very

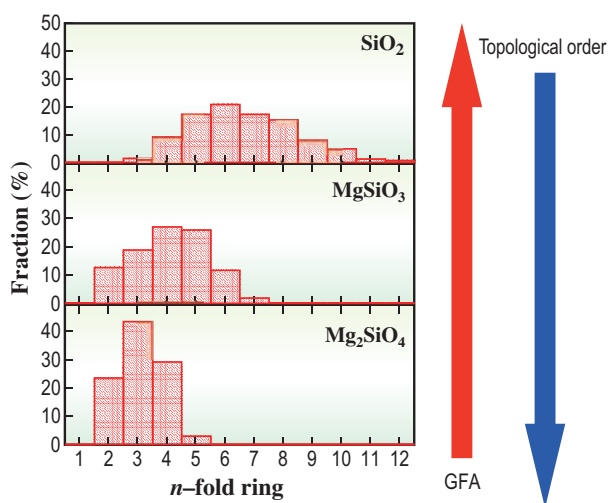


Fig. 2 The distribution of “-Si(Mg)-O-Si(Mg)-O-Si(Mg)-” rings in MgSiO_3 and Mg_2SiO_4 glasses and the distribution of “-Si-O-Si-O-Si-” rings in SiO_2 glass.

ambiguous owing to the lack of long-range periodicity manifested by a broad diffraction pattern. However, a combination of synchrotron X-ray diffraction measurements and theoretical simulations is a powerful technique for studying the relationship between atomic/electronic structure and physico-chemical properties, which is crucial for revealing and understanding the origin of unique functional properties in disordered materials.

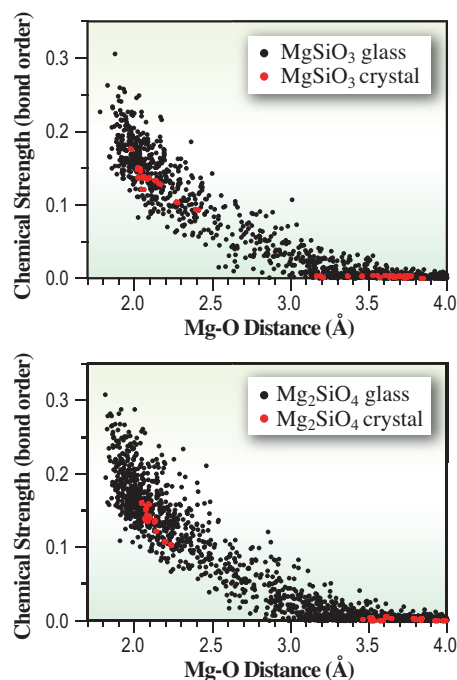


Fig. 3. Scatter plot of the chemical bond order as a function of distance for Mg-O pairs in MgO-SiO_2 glass. The crystalline reference values are included in red. [2]

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References

- [1] S. Kohara, H. Ohno, M. Takata, T. Usuki, H. Morita, K. Suzuya, J. Akola and L. Pusztai: *Phys. Rev. B* **82** (2010) 134209.
- [2] S. Kohara, J. Akola, H. Morita, K. Suzuya, J.K.R. Weber, M.C. Wilding and C.J. Benmore: *Proc. Nat. Acad. Sci. USA* **108** (2011) 14780.
- [3] P.K. Gupta and A.R. Cooper: *J. Non-Cryst. Solids* **123** (1990) 14.
- [4] K. Shimoda *et al.*: *Am. Mineral.* **92** (2007) 695.
- [5] S. Sen *et al.*: *J. Phys. Chem. B* **113** (2009) 15243.