Glass Forming at Limit:
How Glass Forms when there is Insufficient Network Former ?

Vitreous forsterite (v-Mg_2SiO_4) is an important "prototypical" orthosilicate in the earth's magmas in the upper mantle and a model system for non-equilibrium low-silica-content binary melts. Experimental studies remain difficult due to the high melting point (~2150 K) and instability of forming a bulk glass. The low (33.33 mole%) SiO_2 content in v-Mg_2SiO_4 effectively prevents the formation of an extended SiO_4-based network, hence an interpretation based on the model structure of conventional silicate glasses. v-Mg_2SiO_4 can be considered as an extremely fragile glass as opposed to the strong characteristic of SiO_2-rich silicate network glasses [1]. Information regarding the structure of v-Mg_2SiO_4 is important for the development of refractory and laser host materials, formation of interplanetary and interstellar dust, prediction of thermodynamical properties of olivine minerals, and advancement of phenomenological theory of glass formation.

Experiments using the shock pressurization of olivine or the splat quenching of forsterite resulted in samples that contained a few percent glass. Only until recently Mg_2SiO_4-composition glasses prepared by containerless melting are available for structural characterization. In the present work, combined neutron and high-energy X-ray diffraction data obtained at
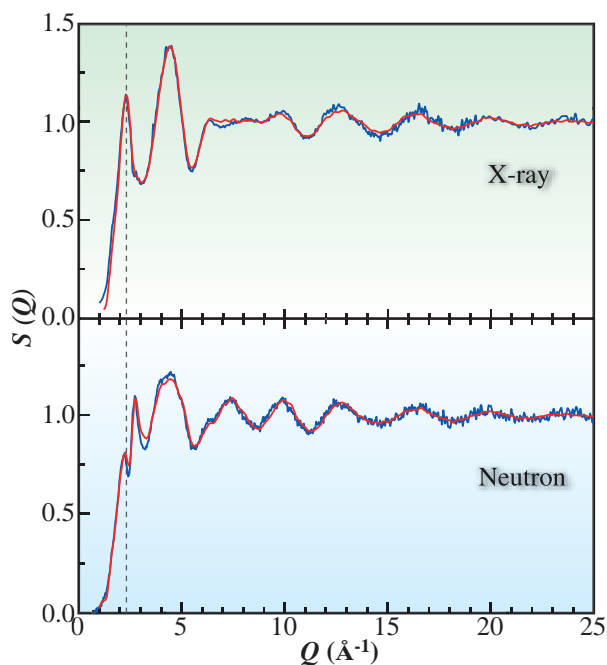

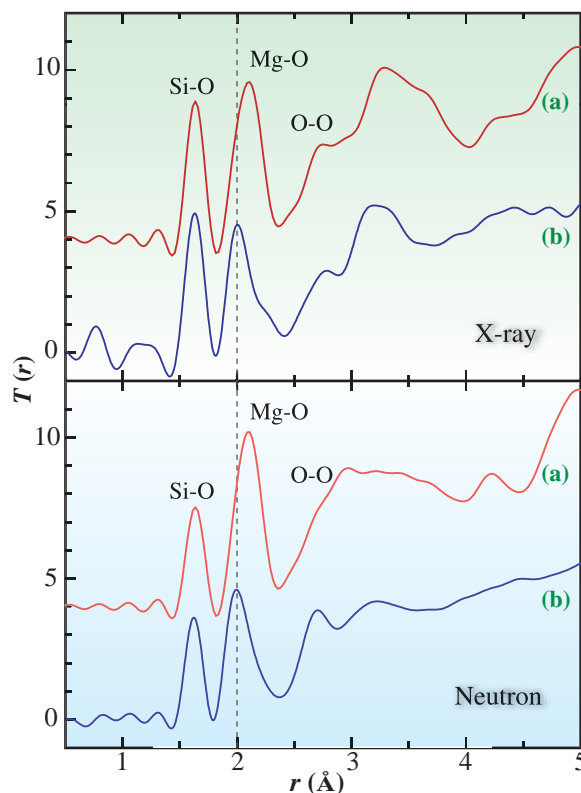Fig. 2. Total correlation functions $T(r)$ of c-Mg_2SiO_4 **(a)** and v-Mg_2SiO_4 **(b)**. The curves of the crystal were calculated using the PDFFIT computer code according to the forsterite crystal structure. For clarity, they are displaced upward by 4 units from the baseline. The unphysical oscillations below 1.5 Å arose mainly from the Fourier transformation of truncated data at a finite Q.

Fig. 1. Total structure factors $S(Q)$ of v-Mg_2SiO_4 (blue: experimental data; red: RMC simulation).

beamline **BL04B2** and reverse Monte Carlo (RMC) modelling [2] were applied to the study of a bulk Mg_2SiO_4-composition glass formed by containerless processing of small droplets of a molten precursor [1].

The measured neutron and X-ray structure factors, $S(Q)$, [3] of bulk Mg_2SiO_4-composition glasses are shown in Fig. 1. The higher Q position (~2.2 Å^{-1}) of the first sharp diffraction peak than those in vitreous silica and typical non-orthosilicate glasses and melts (below 1.8 Å^{-1}) [4] indicates that v-Mg_2SiO_4 has a unique short-range order structure.

The derived total correlation functions, $T(r)$, are shown in Fig. 2. The well-resolved peak profiles corresponding to the Si-O and Mg-O nearest neighbors reveal details of the short-range order structure. The Si-O peak is sharp and symmetric and the Si-O coordination number, N_{Si-O}, is 4.05 ± 0.10, which indicates the presence of 4-oxygen coordinated silicon atoms as relatively regular SiO_4 tetrahedra typically found in silicate

glasses. The Mg-O peak in $T(r)$, on the other hand, is broad and skewed towards the high-r side, indicating a distribution of Mg-O distances from 1.8 to 2.5 Å due to highly distorted MgO_x polyhedra. The average N_{Mg-O} is 4.95 ± 0.20. This Mg-O peak differs markedly from that of crystalline forsterite, c-Mg_2SiO_4, (Fig. 2). The shift of the Mg-O peak towards smaller distances in v-Mg_2SiO_4 clearly implies a general relaxation of the MgO_6 octahedra of the crystalline state to include short Mg-O bonds corresponding to MgO_4 and MgO_5 local coordinations. The secondary shoulder near the nominal Mg-O bond length of crystalline MgO_6 octahedra and the tail at larger distances indicate an extensive distortion of polyhedra that include long Mg-O bonds.

To obtain a 3D representation of the glassy structure, particularly the "global" connectivity of SiO_4 and MgO_x polyhedra, we supplemented the measured data with computer simulation of diffraction data using the reverse Monte Carlo (RMC) technique. The converged configuration of the ensemble produced the calculated neutron and X-ray total structure factors $S(Q)$ that agree well with the experimental data

(see Fig. 1). Figure 3(a) shows a distribution of relatively regular SiO_4 tetrahedra, about 33% of which are isolated units. The remaining SiO_4 tetrahedra are connected to form corner-sharing dimers. There are almost no SiO_4 chains or cross-linked networks, in sharp contrast to the extensive 3D SiO_4 networking features in vitreous silica or in many silica-rich binary glasses. The Mg-O atoms, on the other hand, show a well-connected assembly featuring both edge- and corner-sharing MgO_x polyhedra (Fig. 3(b)). We found the presence of MgO_x polyhedra of x = 4, 5 and 6 corresponding to approximately the ratio of 3:5:2 according to the RMC snapshot representing the best fit of the data. Figure 3(c) shows a typical network element of MgO_x polyhedra. The MgO_4 units are relatively uniform tetrahedra whereas the MgO_5 and MgO_6 units have long mean bond lengths and contain one or two long bonds (observed as the shoulder and tail in Fig. 2).

Our findings concerning the glassy structure at the limit of insufficient network former have broad implications in the use of unconventional network former/modifier ratio in glass materials that may form new environments for dopant ions and offer potentials for tailored optical and electronic properties. In addition, the knowledge of the structure of glassy forsterite will aid in understanding the present and past magmatic processes in the earth's and moon's mantle. The present study of an unusual glass prepared by the containerless method may provide insights into the highly non-equilibrium material processing that occurs in interplanetary and interstellar environments [5].
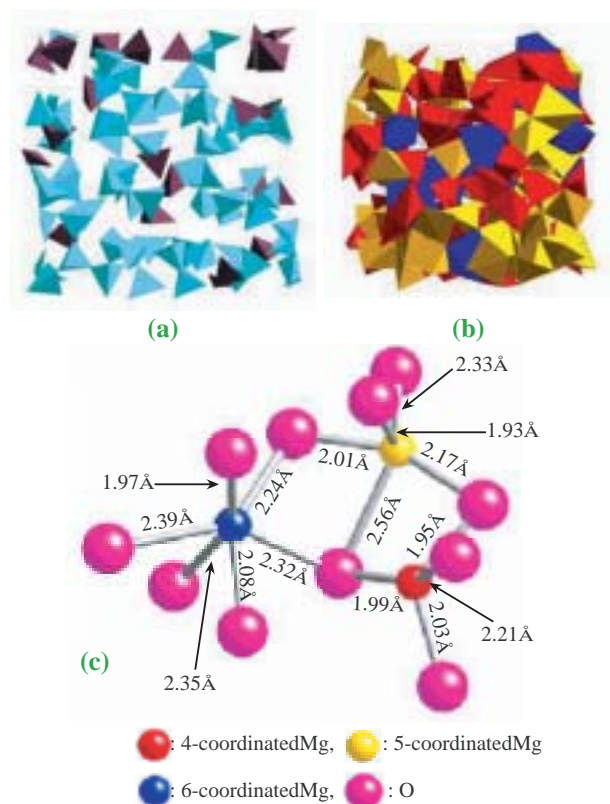

(a)   (b)

(c)

: 4-coordinated Mg,   : 5-coordinated Mg
: 6-coordinated Mg,   : O

Fig. 3 **(a)** Configuration of SiO_4 tetrahedra obtained from the RMC snapshot. About 33% of tetrahedral are unconnected (purple). The remaining SiO_4 units are joined by an oxygen atom to form dimers (blue). **(b)** Network configuration of MgO_x polyhedra, x = 4 (red), 5 (yellow) and 6 (blue). The majority are MgO_5 units. **(c)** Typical network element containing MgO_4, MgO_5, and MgO_6 units obtained from the RMC snapshot.

Shinji Kohara[a,*], Kentaro Suzuya[b] and Ken Takeuchi[c]

(a) SPring-8 / JASRI
(b) Neutron Science Research Center, Japan Atomic Energy Research Institute (JAERI)
(c) Faculty of Industrial Science and Technology, Tokyo University of Science

*E-mail: kohara@spring8.or.jp

References

[1] J.A. Tangeman *et al.*: Geophys. Res. Lett. **28** (2001) 2517.
[2] R. L. McGreevy: J. Phys Condens. Matter. **13** (2001) R877.
[3] *S. Kohara, K. Suzuya, K. Takeuchi, C.-K. Loong, M. Grimisditch, J.K. Weber, J.A. Tangeman, T.S. Key: Science **303** (2004) 1649.*
[4] S. Kohara and K. Suzuya: Nucl. Instrum. Meth. B **199** (2003) 23.
[5] F.J. Molster *et al.*: Nature **401** (1999) 563.