Electronic Supplementary Information for: Deformability of Mg-Aluminosilicate glass under High Pressure and Shear Stress: Dynamic Coordination Change of Al^{3+}

Kosei Osada[a], Akihiro Yamada[a, b], Koji Ohara[c], Satoshi Yoshida [a, b] and Jun Matsuoka [a, b]

a) Department of Materials Chemistry, The University of Shiga Prefecture,
Hassaka-cho, Hikone, Shiga 522-8533, Japan
b) Center for Glass Science and Technology, The University of Shiga Prefecture,
Hassaka-cho, Hikone, Shiga 522-8533, Japan
c) Diffraction and Scattering Division, Japan Synchrotron Radiation Research Institute (JASRI),
Sayo-gun, Hyogo, 679-5198, Japan.

Corresponding author: Akihiro Yamada,
Email: yamada.ak@mat.usp.ac.jp

Pressure-cell setup of the high-pressure deformation experiment

The glass sample, prepared as described above, was positioned at the center of the high-pressure cell shown in Fig. S1. To apply a simple shear stress, the sample was sandwiched between a pair of 45°-cut alumina pistons. Along the compression axis, SUS303 stainless steel and (Mg,Cr)O were used as backing materials, and the applied shear stress was controlled by varying the thickness of these components. The sample was enclosed by a graphite ring, and the entire assembly of sample and pistons was surrounded by an MgO sleeve. This assembly was then placed inside a boron-epoxy pressure medium, which was supported by an outer PTFE ring to prevent collapse during loading.

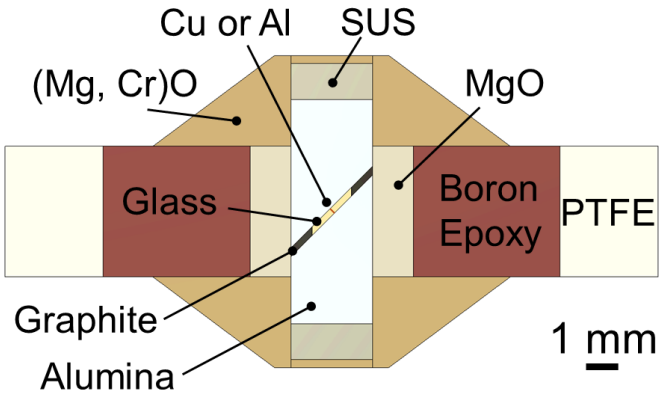

Fig. S1. A cross section of the cell assembly used in the deformation experiment of the modified Paris-Edinburgh anvils system. The compression axis is vertical axis (see ref: 15 on the detail of the compression geometry).

Baseline subtraction of Raman Spectroscopy

The spectra of the deformed samples exhibited a background, which was corrected by baseline subtraction, as illustrated in Fig. S2.

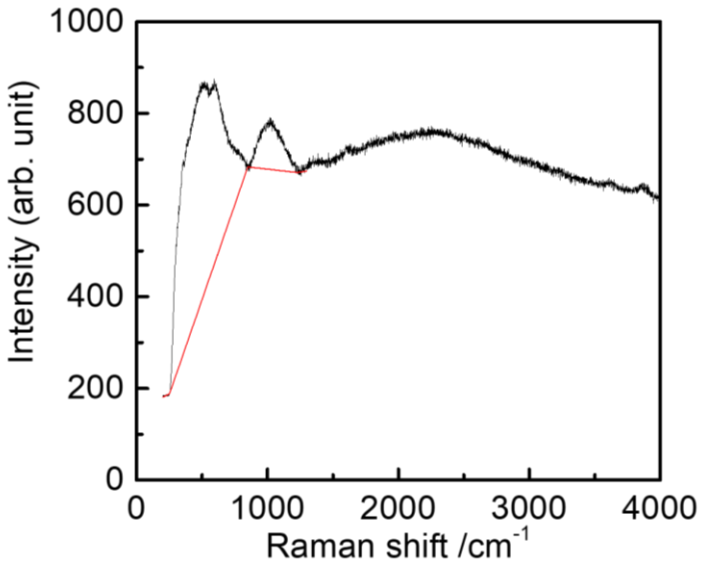

Fig.S2 Example for the background correction in Raman spectra. Black line and red line indicate Raman spectra and baseline, respectively. Region at 0-1300 cm^{-1} is spectrum of glass, and 1300-4000 cm^{-1} is background.

Al coordination number estimation from Al K-edge XANES

To quantify the aluminum coordination states, XANES spectra were deconvoluted following previous studies.[16,17] The results of the analysis are shown in Fig. S3 and Table S1. Note that this analysis only considers two aluminum coordination states, $^{[IV]}$Al and $^{[VI]}$Al, to avoid over-parameterization.

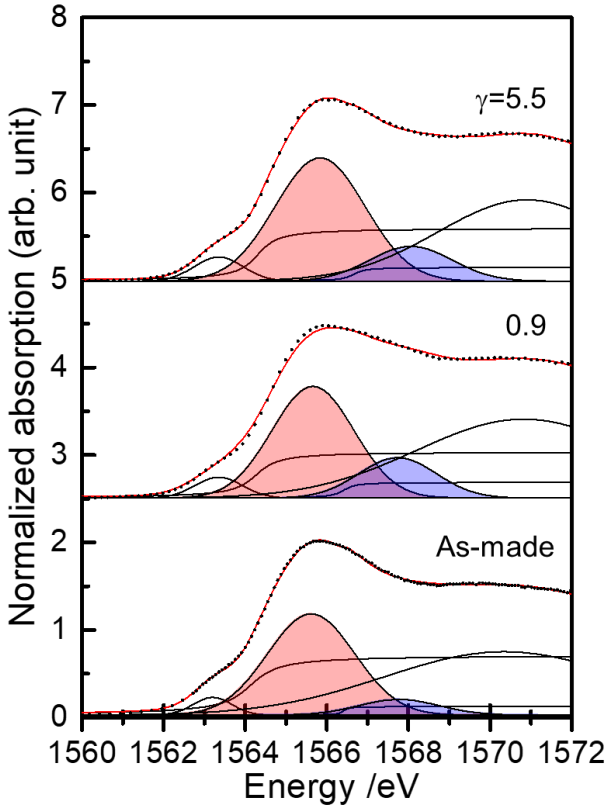

Fig.S3 Al K-edge X ray absorption spectra of as-made and deformed glasses. Dotted lines represent the experimental spectra. Black and red lines correspond to the deconvolution results and the synthesized spectra, respectively. The hatched red and blue components indicate contributions from $^{[IV]}$Al and $^{[VI]}$Al, respectively.

Table S1 Fitting parameters of deconvoluted peaks in XANES spectra of the glasses

Shear strain, γ	AlO_4			AlO_6			Third peak		
	Position /eV	FWHM /eV	Area	Position /eV	FWHM /eV	Area	Position /eV	FWHM /eV	Area
0	1565.6	2.5	3.1	1567.8	2.3	0.4	1570.3	6.9	5.3
0.92	1565.7	2.4	3.2	1567.7	2.2	1.1	1570.8	6.2	5.9
3.94	1565.7	2.5	3.6	1567.7	2.4	0.6	1570.6	5.5	4.7
4.80	1565.7	2.5	3.4	1567.9	2.3	0.9	1570.7	4.9	3.8
5.46	1565.8	2.6	3.9	1568.1	2.4	1.0	1570.9	5.1	5.1

Mg K-edge X-ray Absorption Near-Edge Spectroscopy (XANES)

Mg K-edge XANES measurements were performed at the BL-13 beamline of the Ritsumeikan University SR Center. White synchrotron radiation was monochromatized using a KTP(011) crystal and directed onto the sample surface. The spectra were collected over an energy range of 1250–1350 eV in fluorescence yield mode, using a Silicon Drift Detector (SDD) positioned at 90° to the incident beam. The energy scale was calibrated by setting the K-edge peak of a reference MgO sample to 1311.3 eV. The collected spectra were then deconvoluted using a Gaussian function and an arctangent step-function. The raw spectrum and the result of this deconvolution are shown in Fig. S4a.

The position of the deconvoluted Mg K-edge peak has been reported to correlate with the magnesium-oxygen bond distance.[54] The peak position observed in our samples corresponds to that of six-fold coordinated Mg (Fig. S4b). Although the peak position shifted slightly to a lower energy with increasing strain, the total shift was less than 0.1 eV. This corresponds to an estimated change in bond distance of only ~0.01 Å. Therefore, it is concluded that no significant change in the Mg coordination number occurred as a result of the deformation.

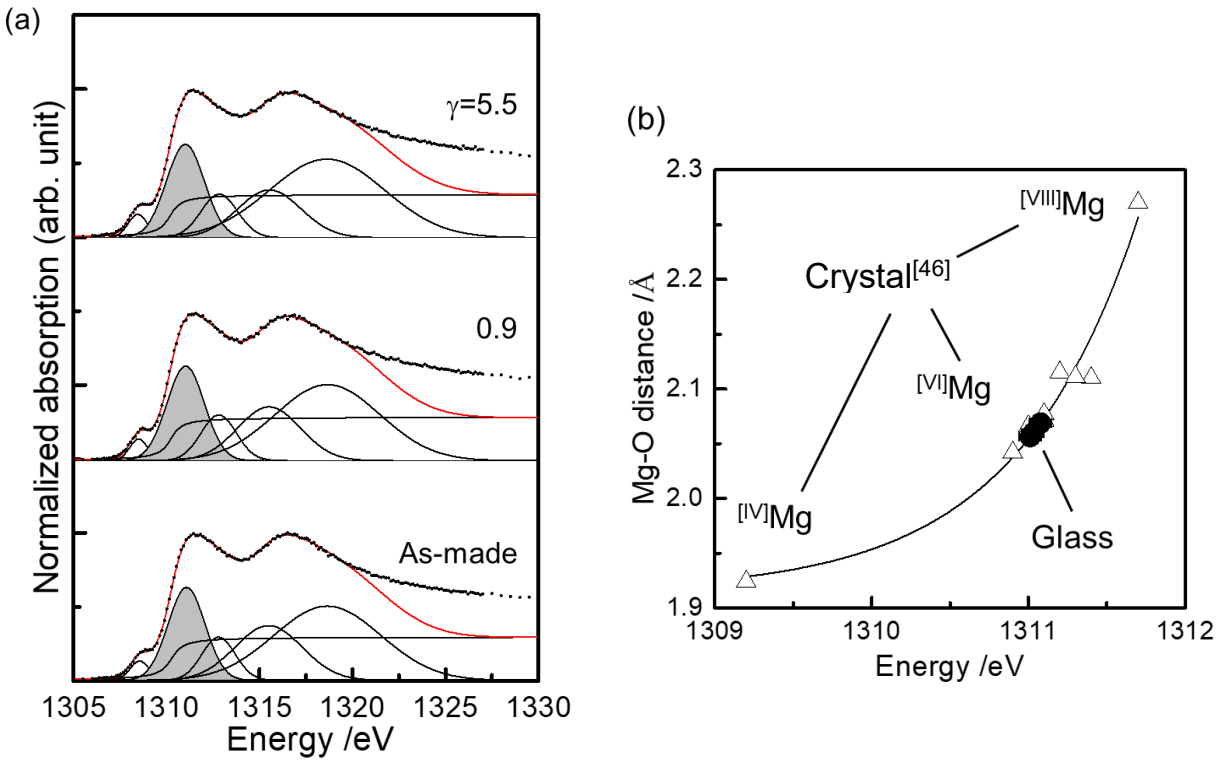

Fig. S4 (a) Mg *K*-edge XANES spectra of MAS glasses. Solid dots indicate XANES spectrum. Black and red lines show deconvoluted peaks and sum of ones. Gray hatch indicates peak A. (b) Calibration curve for Mg-O distance from Ref: 46 (triangles). Solid symbols are this work.

Determination of Defect Concentration by Electron Spin Resonance Spectroscopy

Baseline correction was applied to the raw spectra (Fig. S5a), and the intensity profiles were subsequently integrated and normalized to the Mn^{2+}/MgO peak (Fig. S5b, diamond) prior to calculating spin concentrations. Spin concentrations were determined from the double integration of the signal (Fig. S5b, red hatch). A calibration curve for spin concentration was obtained using solutions of TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl) in dehydrated benzene at different concentrations. Examples of baseline-corrected ESR profiles of TEMPOL and the glass are shown in Fig. S5c and S5d, respectively.

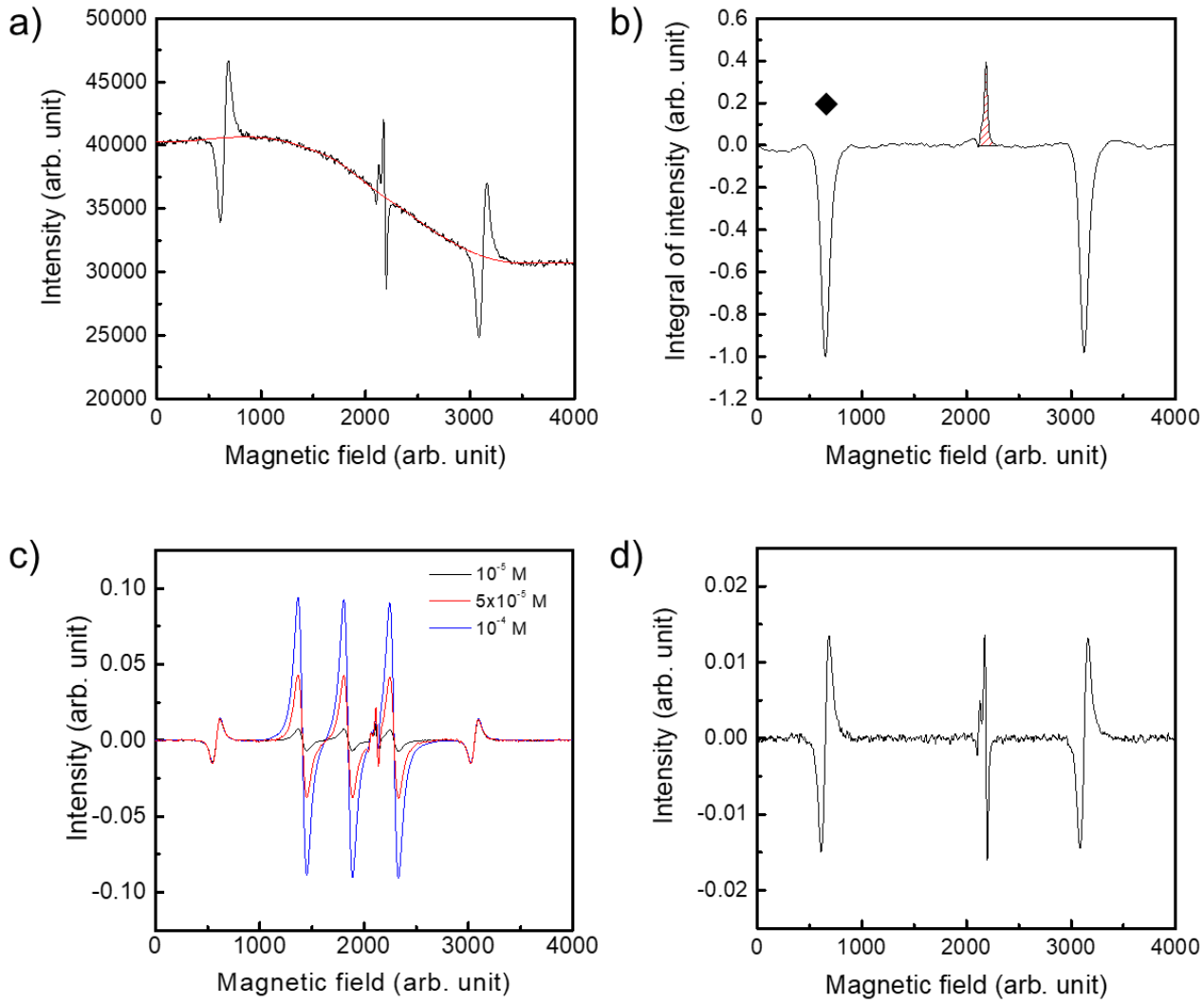

Fig. S5 (a) Raw ESR signal (black line) and baseline (red line) for the glass sample. (b) Integrated profile of the glass after baseline correction and intensity normalization. The red hatch and diamond indicate the double integration of the sample ESR signal and the Mn^{2+}/MgO peak, respectively. (c) Examples of ESR signals of TEMPOL after baseline correction and intensity normalization. (d) An example of the ESR signal of the glass sample after baseline correction and intensity normalization.