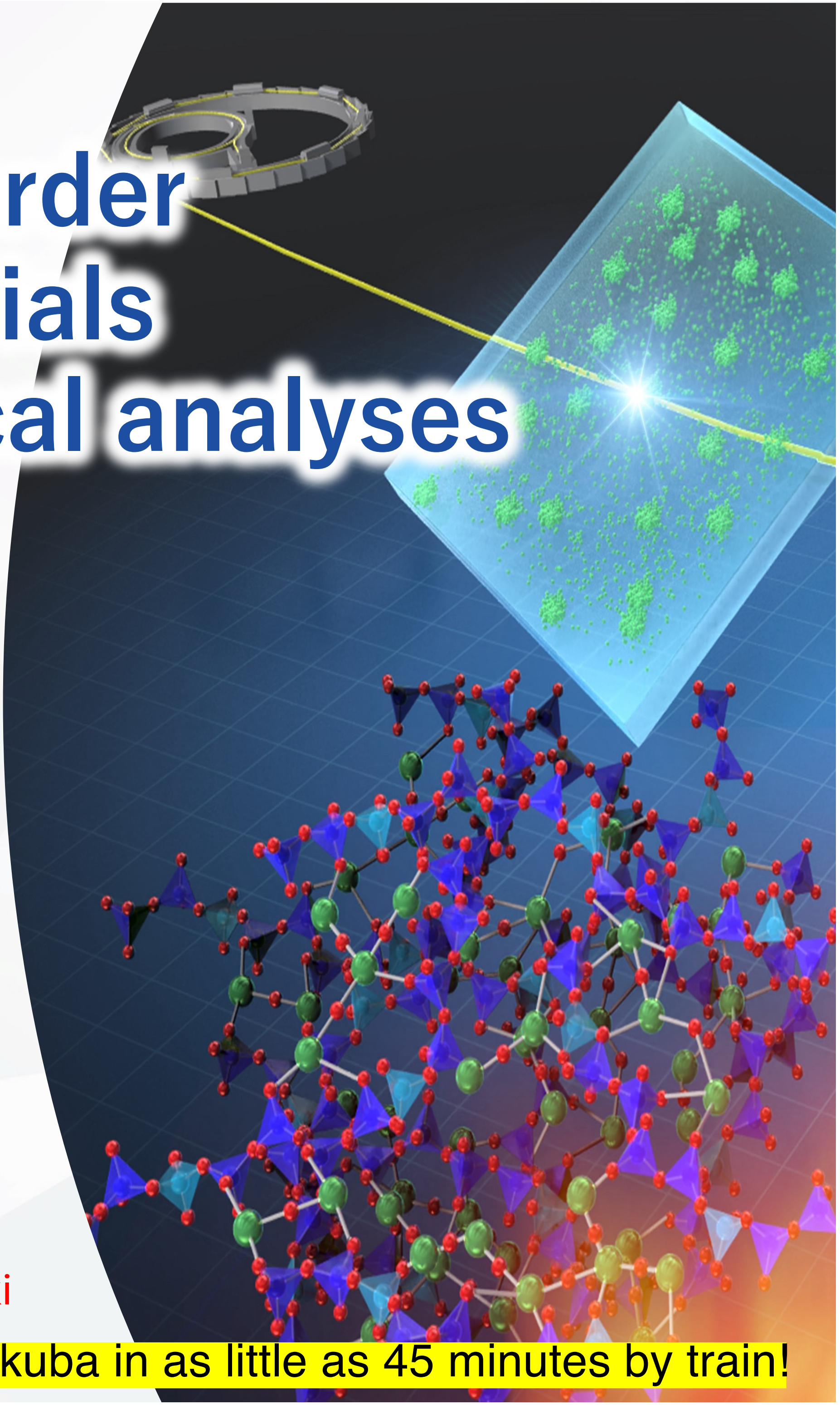
Intermediate-range order in glassy oxide materials revealed by topological analyses



Yohei ONODERA

Quantum beam diffraction group,
Center for Basic Research on Materials (CBRM),
National Institute for Materials Science (NIMS)

Tsukuba, Ibaraki

You can get from Tokyo to Tsukuba in as little as 45 minutes by train!

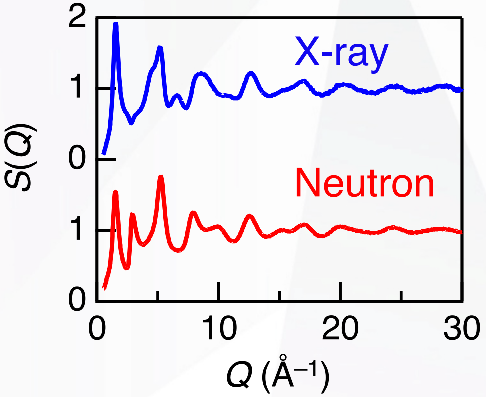
Quantum beam diffraction group @CBRM/NIMS

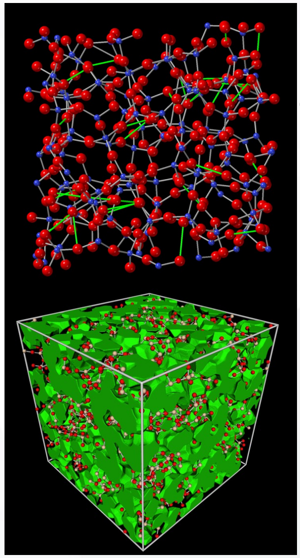
Kohara (GL)

Onodera

1) Extracting order hidden in disordered structures via topological analysis

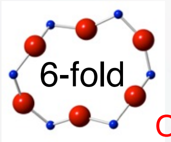
Silica (SiO_2) glass





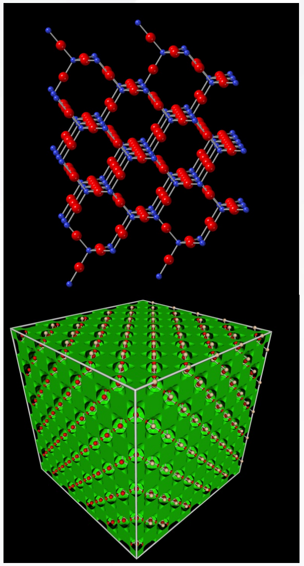
cavity

Comparable with crystal structures

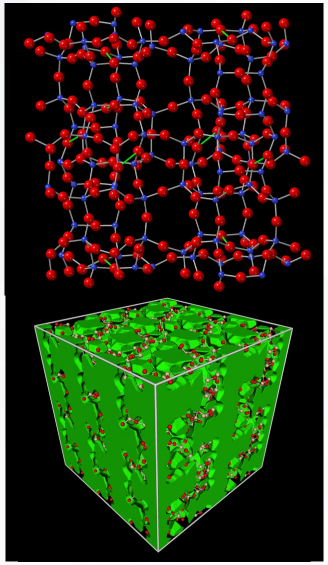


ring

β-cristobalite



MFI (Zeolite）

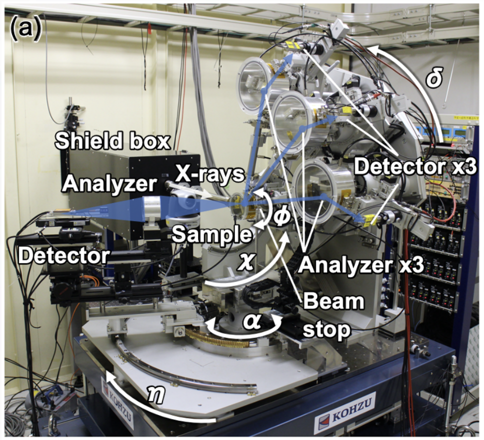


S. Kohara *et al.*, *J. Ceram. Soc. Jpn.* **132**, 653 (2024).

2) Application of element-specific measurement to materials

Anomalous X-ray scattering

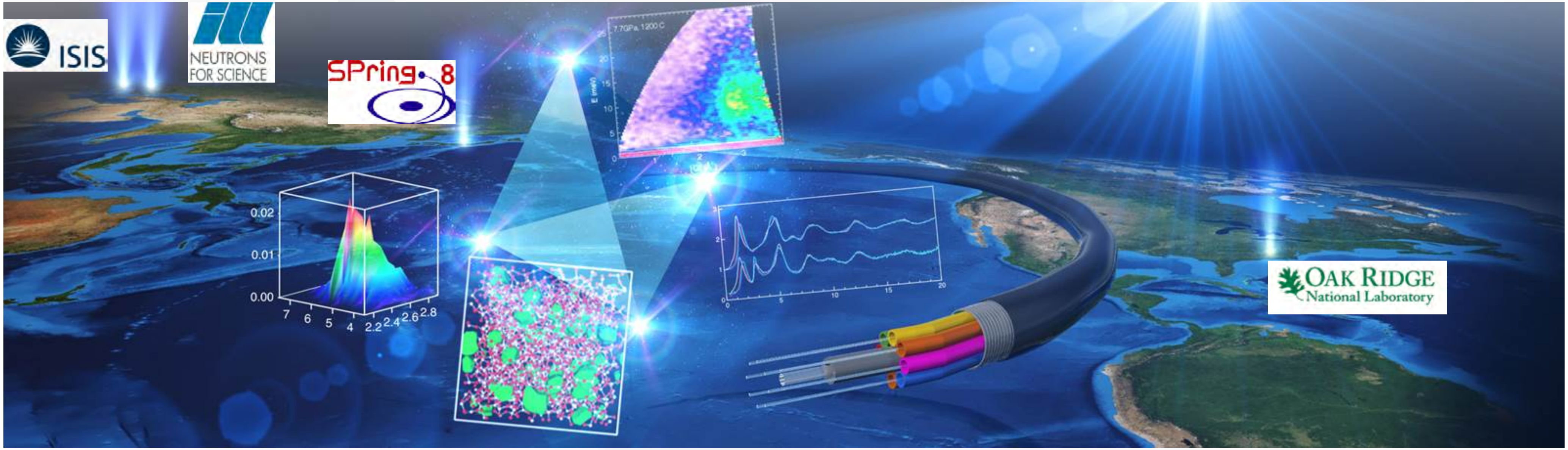
✔A new diffractometer for anomalous X-ray scattering developed jointly with JASRI at SPring-8



H. Tajiri *et al.*, *J. Synchrotron Rad.*, **32**, 125 (2025) .

with Prof. Phil. Salmon

The structure of densified silica glass



Y. Onodera *et al.*, *NPG Asia Mater.*, 12, 85 (2020).
“Structure and properties of densified silica glass:
characterizing the order within disorder”

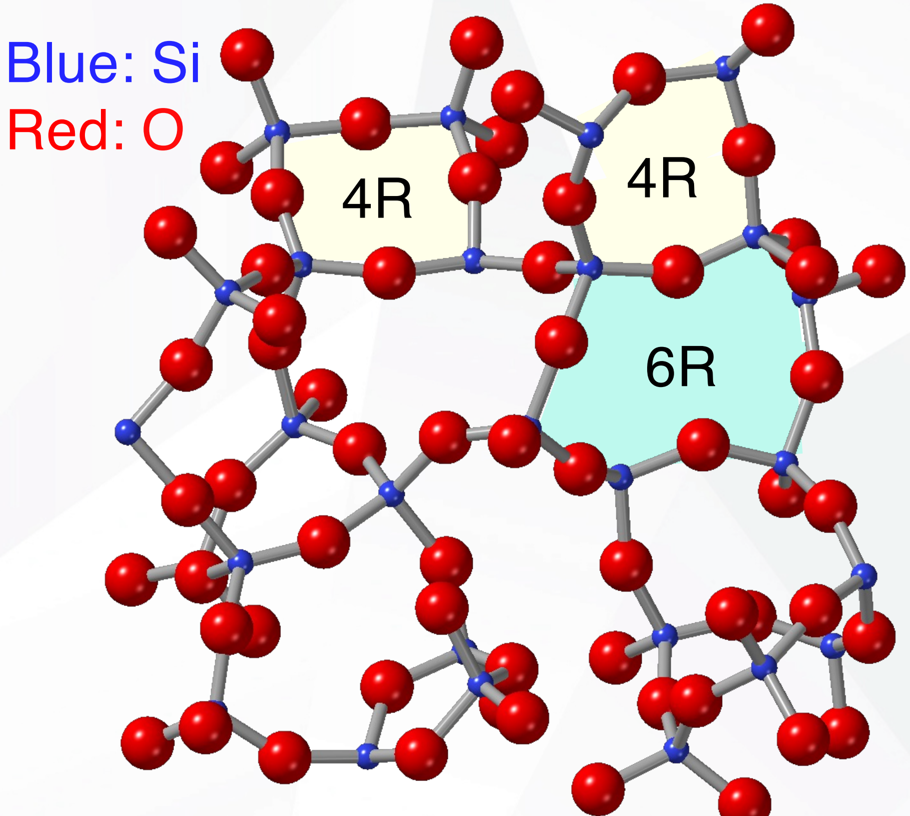
✓ Synthesis of glass with high density and high structural order
→Achieving high density and structural order is crucial for optical fiber glass

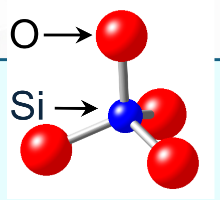
✓ Structural features of the obtained high-density glass were extracted from 3D structural model

Structure of silica (SiO_2) glass

SiO_2: prototypical network-forming oxide material

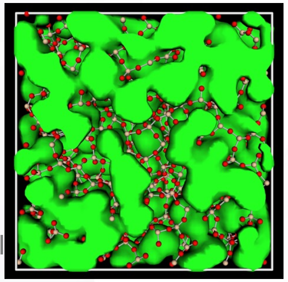
Atomic arrangement of SiO_2 glass





- ✓ $N_{Si–O}=4$, $N_{O–Si}=2$
- ✓ Interconnection of SiO_4 tetrahedra forms a network by sharing of oxygen atoms at the corners
- ✓ Network structure consists of rings of various sizes
- ✓ A large cavity is formed

Small cation–oxygen coordination number and corner-sharing network → good glass-forming ability



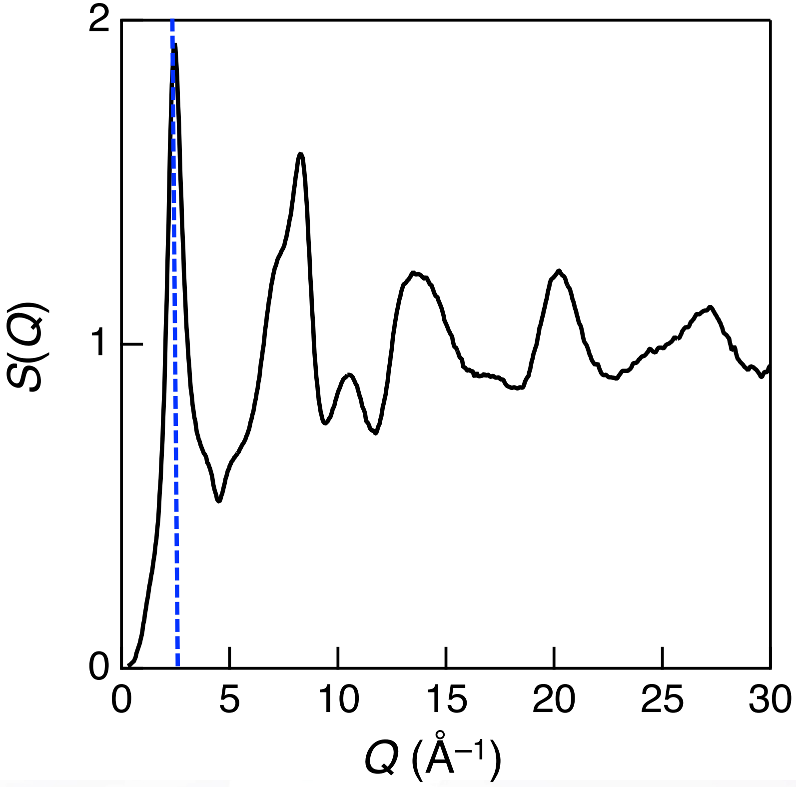
Cavity volume ratio: 32%

S. Kohara and K. Suzuya, *J. Phys.: Condens. Matter*, **17**, S77 (2005).

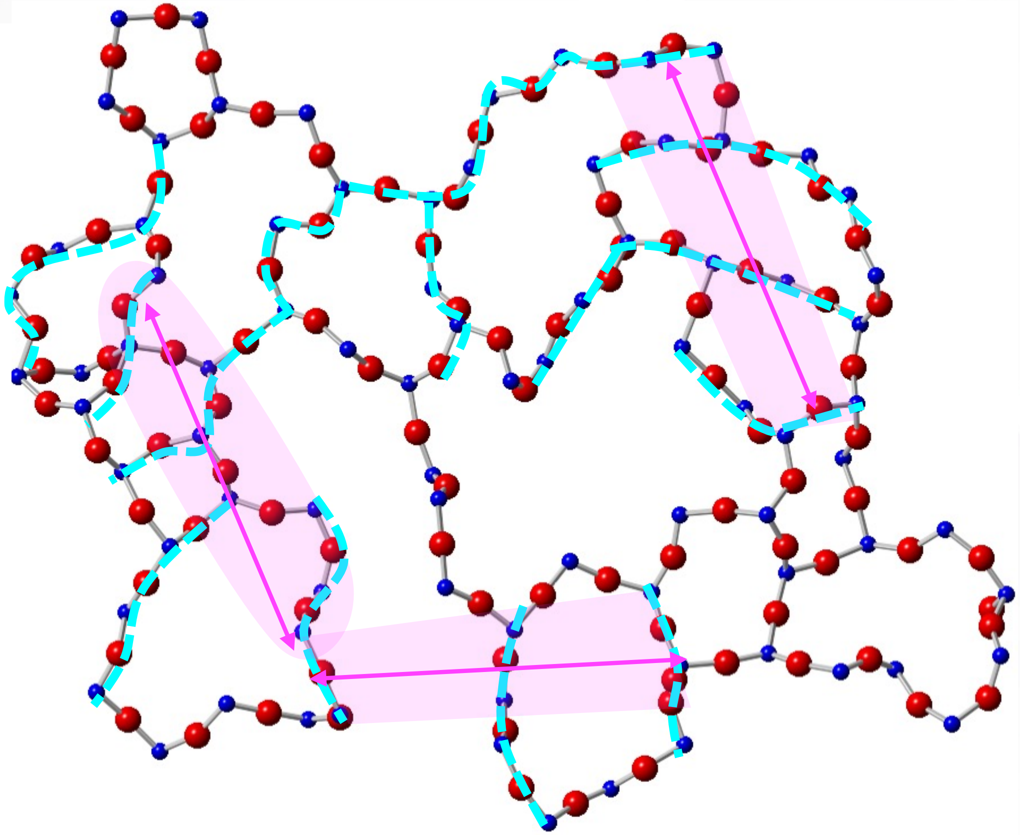
The origin of FSDP in SiO_2 glass

X-ray diffraction data

First Sharp Diffraction peak (FSDP)



Thickness of the cell is approximately 9 Å
and only the atoms belonging to the network are shown



Sparse periodic structure formed by SiO_4 network

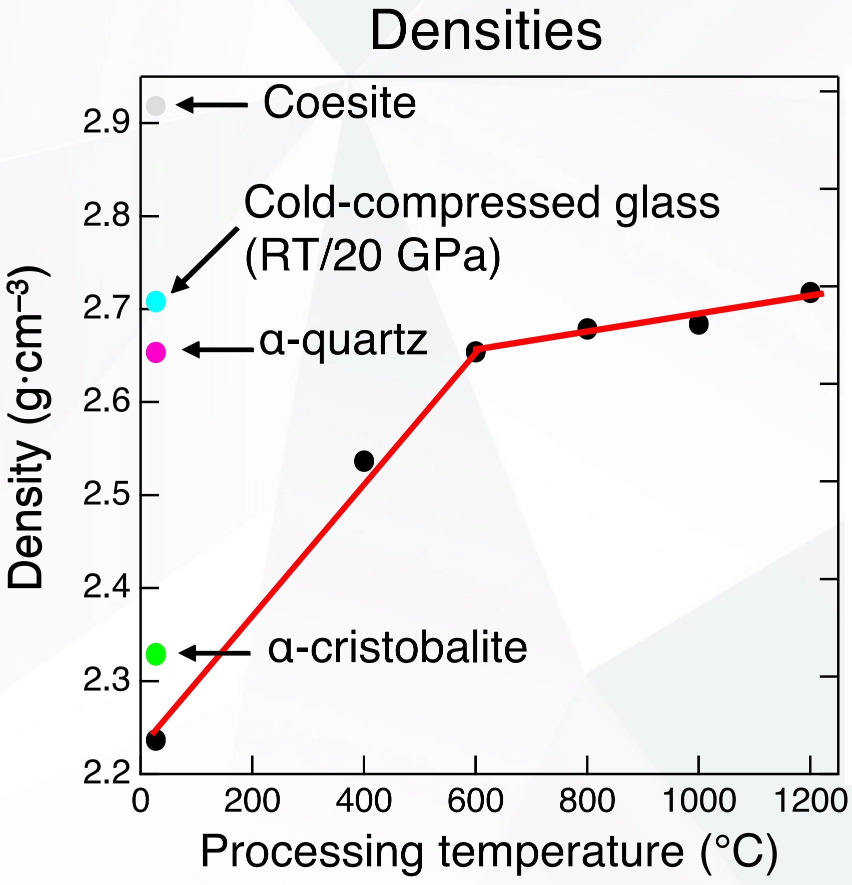
Periodicity: $2\pi/Q_{FSDP}$ ~ 4 Å

Correlation length: $2\pi/\Delta Q_{FSDP}$ ~ 10 Å

S. Kohara *et al.*, *Nat. Commun.*, **5**, 5892 (2014).
Y. Onodera *et al.*, *J. Ceram. Soc. Jpn.*, **127**, 853 (2019).

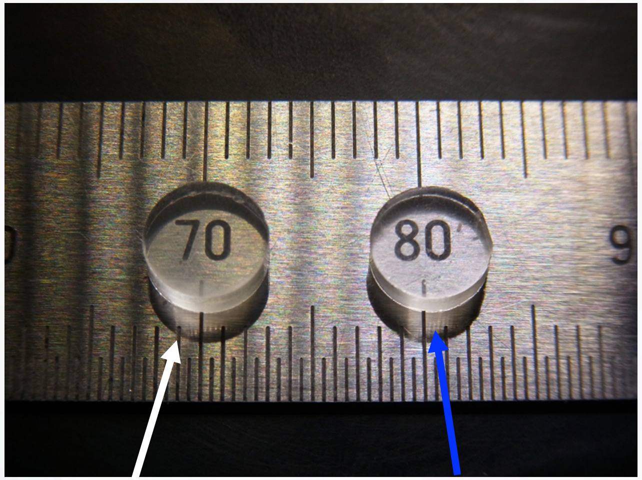
Intermediate-range structure of SiO_2 glass

Densified SiO_2 glasses recovered by hot compression at 7.7 GPa



Black circles: SiO_2 glasses after hot-compression

※The short-range units of cristobalite, quartz, and coesite are all SiO_4 tetrahedra



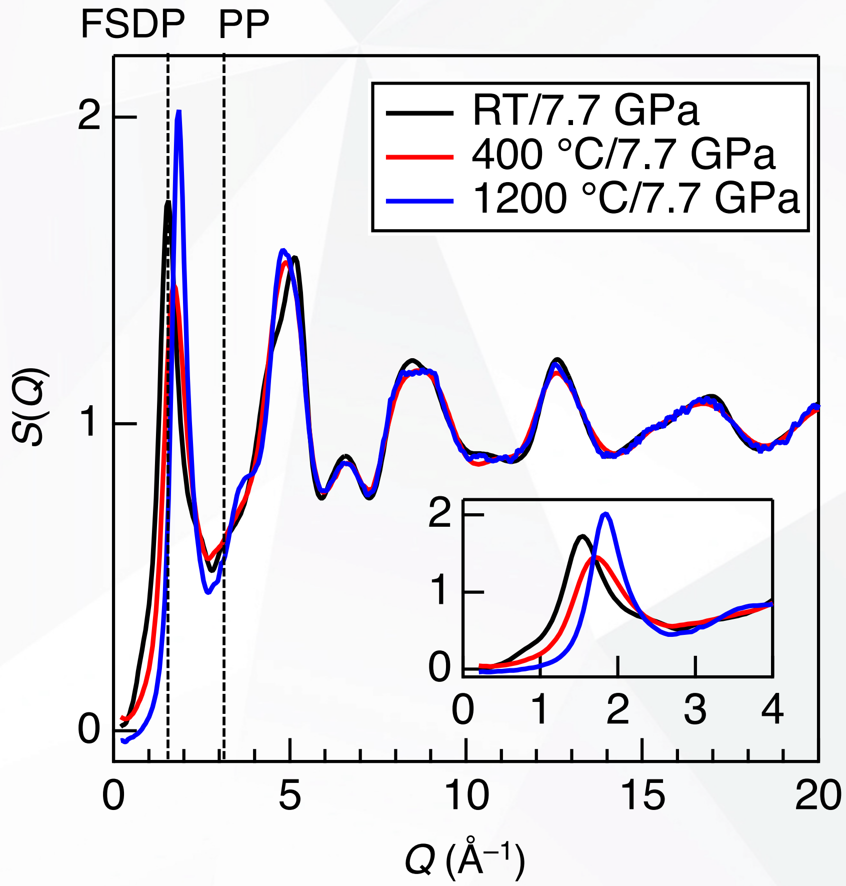
Pristine glass

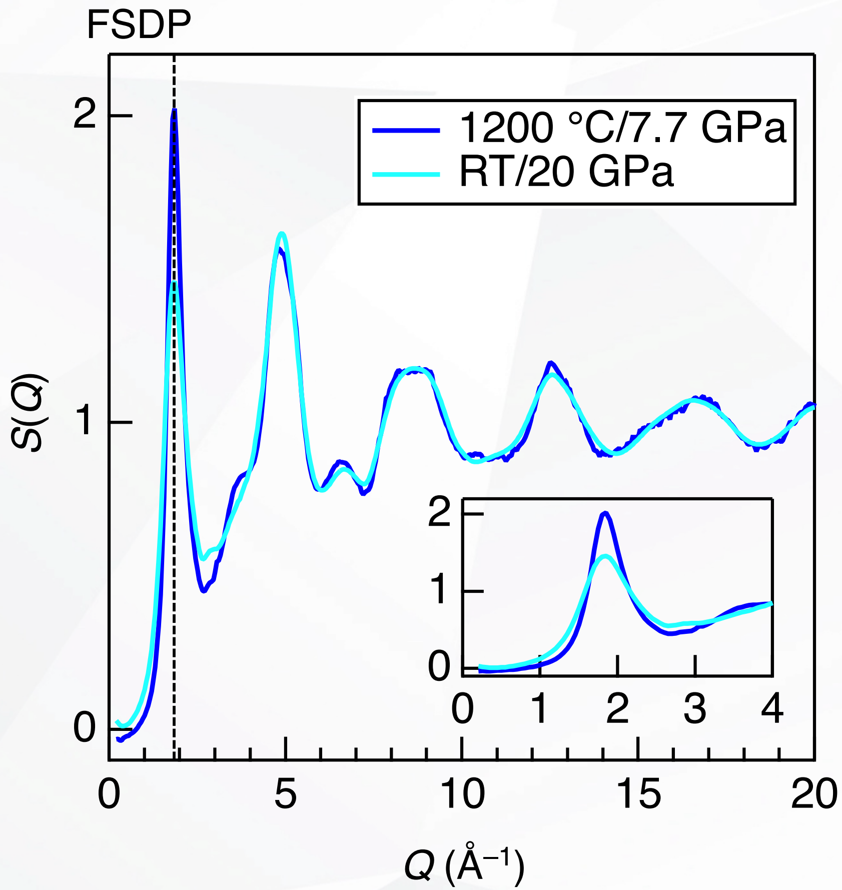
Hot-compressed glass at 1200 °C/7.7 GPa

Hot-compressed glasses were stable for at least 1.5 years at ambient condition

- ✓ Permanently densified SiO_2 glasses were synthesized by hot compression at a pressure of 7.7 GPa and temperatures up to 1200 ˚C
- ✓ Transformation from a low- to high-density amorphous phase ~ 600 ˚C
- ✓ Beyond 1200 ˚C, glass crystalizes into coesite

X-ray structure factors *S*(*Q*) for densified SiO_2 glasses

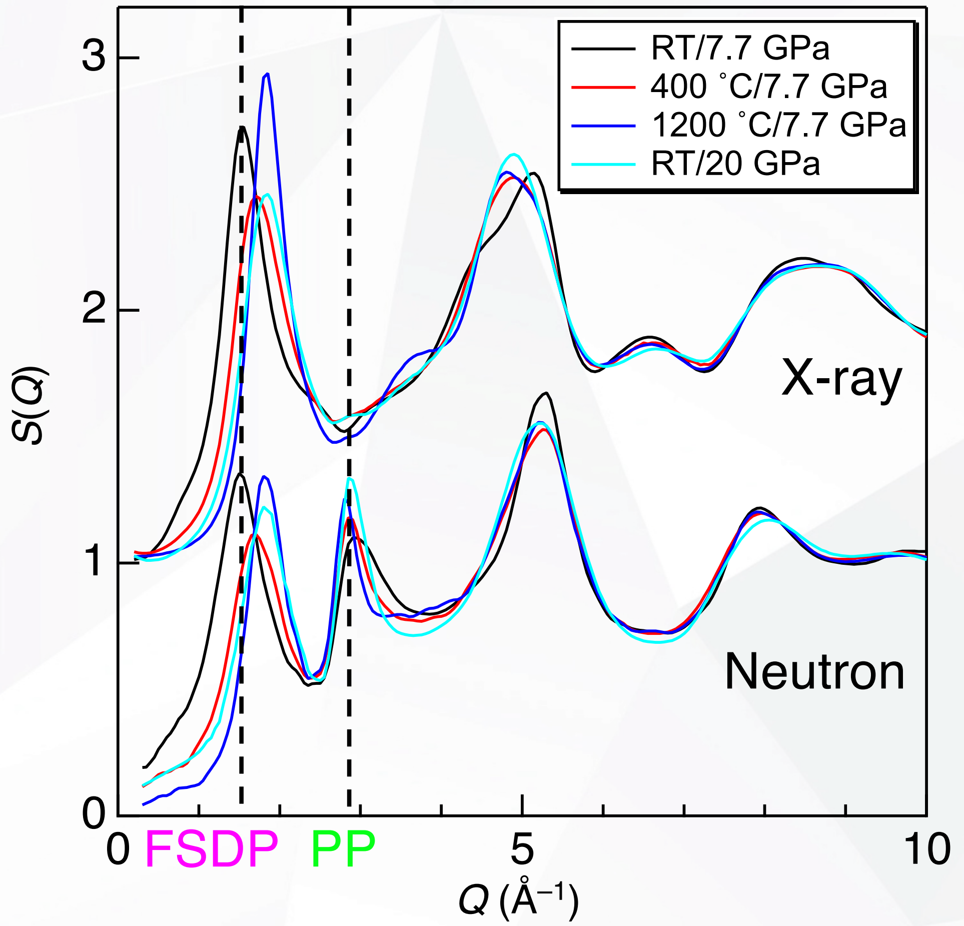




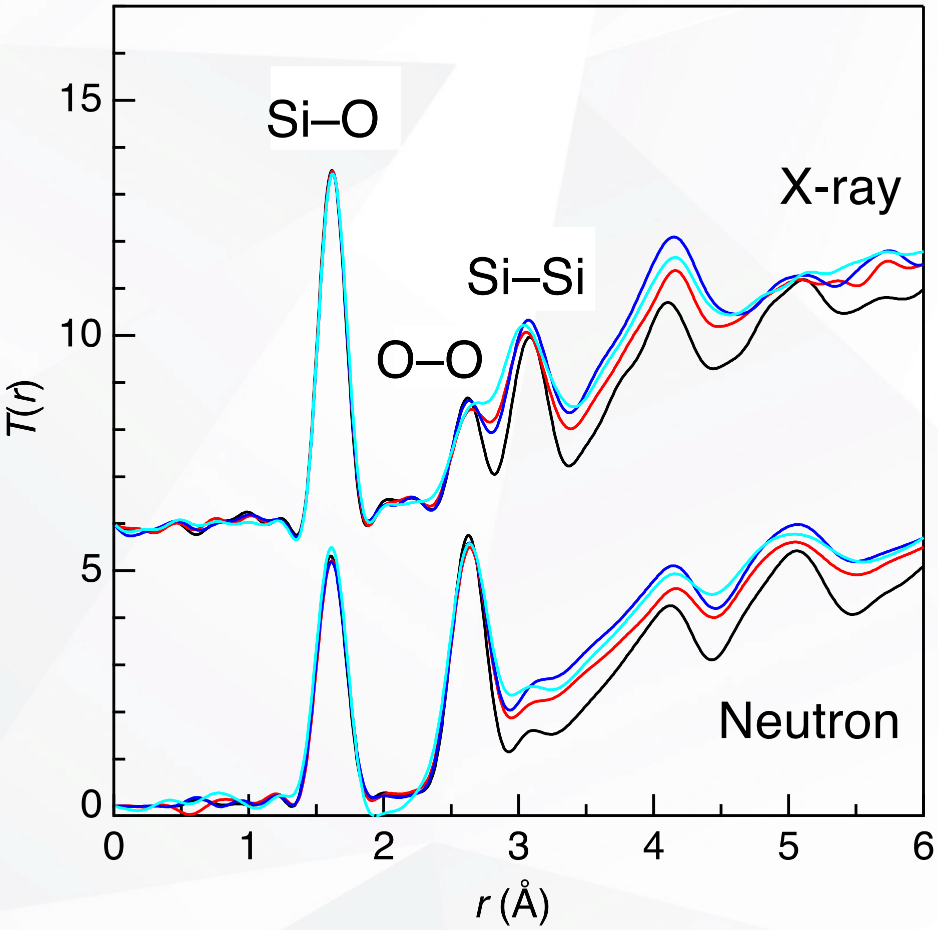
- ✓ The evolution of FSDP at temperature higher than 400 °C is observed (it is consistent with the behavior of density)
- ✓ The height of FSDP of hot-compressed glass (HCG) is greater than that of cold compressed-glass (CCG), although the densities are same

X-ray and neutron diffraction data for densified SiO_2 glasses

Structure factors $S(Q)$



Total correlation functions $T(r)$



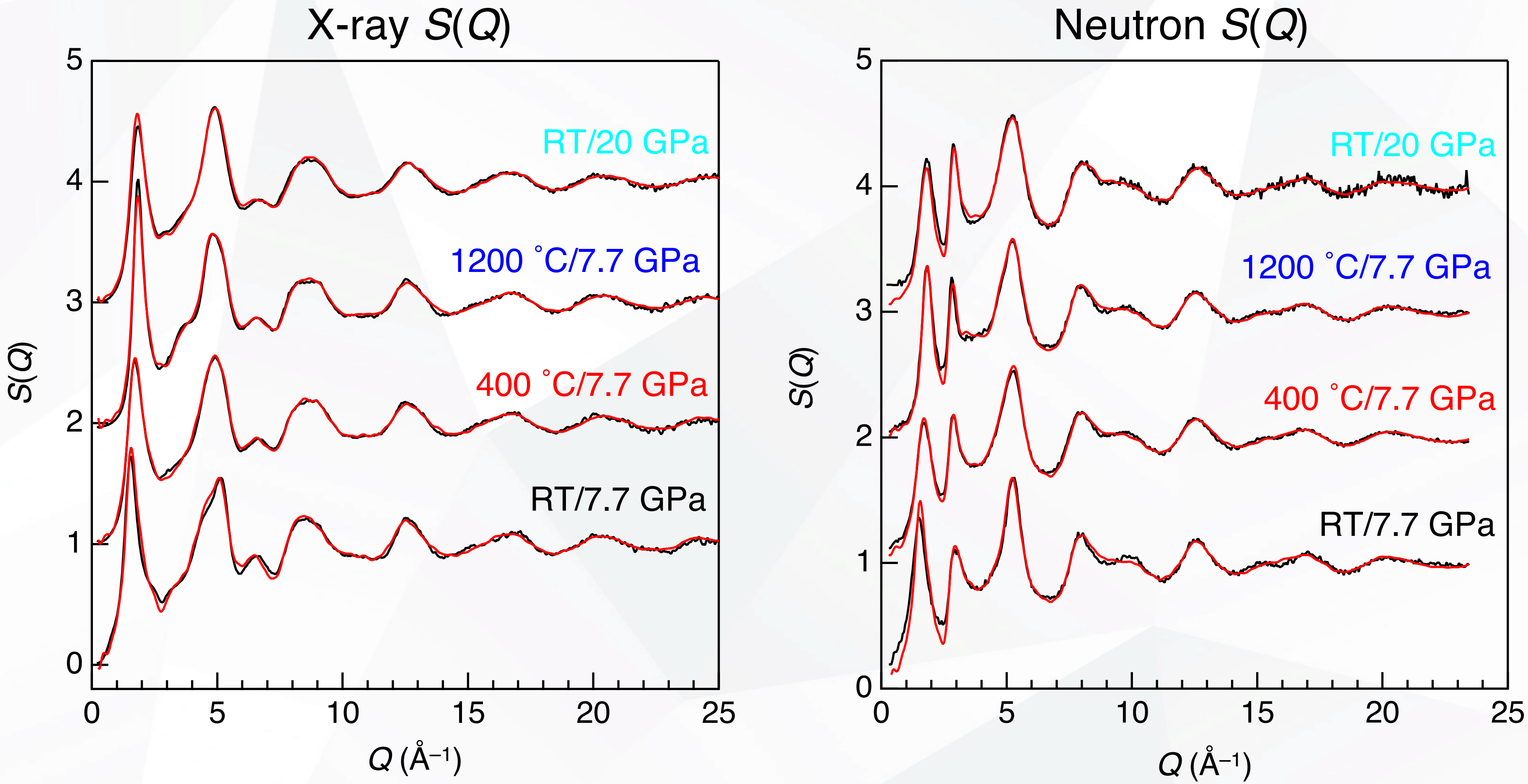
✓ FSDP in X-ray and neutron $S(Q)$ show the similar behavior

Si–O coordination number ~ 4
→ All the glasses sustain a network of corner-sharing SiO_4 motifs

Black: RT / 7.7 GPa, Red: 400 °C / 7.7 GPa, Blue: 1200 ˚C / 7.7 GPa, Cyan: RT / 20 GPa

MD-RMC simulations

Atomic configurations created by classical MD simulations were refined by RMC method



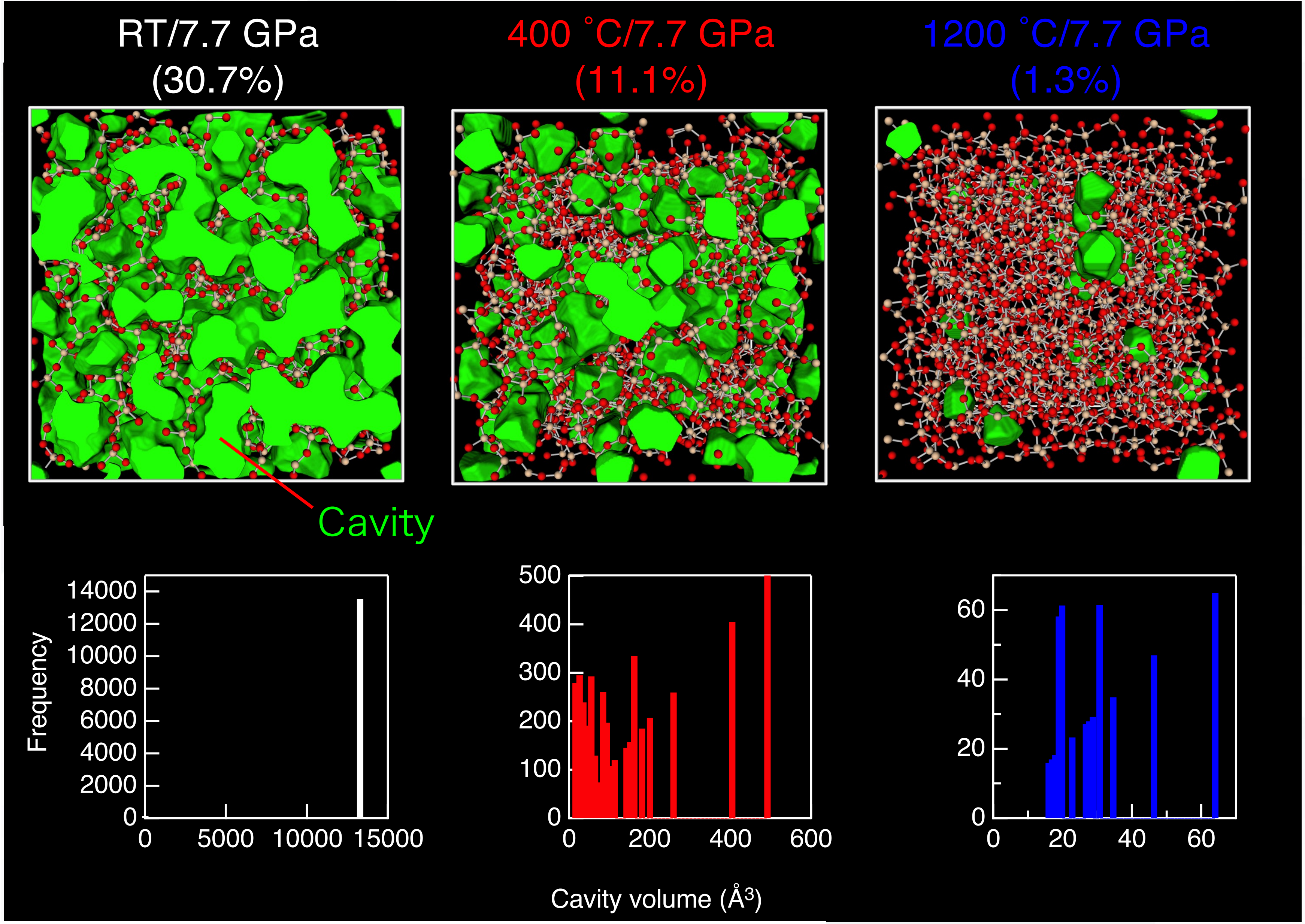
MD-RMC models reproduced measured X-ray/neutron $S(Q)$

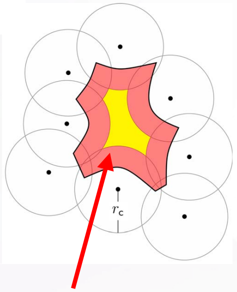
Y. Onodera *et al.*, *NPG Asia Mater.*, **12**, 85 (2020).

Black : experimental data
Red : MD–RMC model

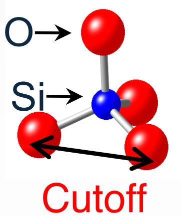
Cavity analysis

*F. Heimbach, et al., *J. Comput. Chem.* **38**, 389 (2017).





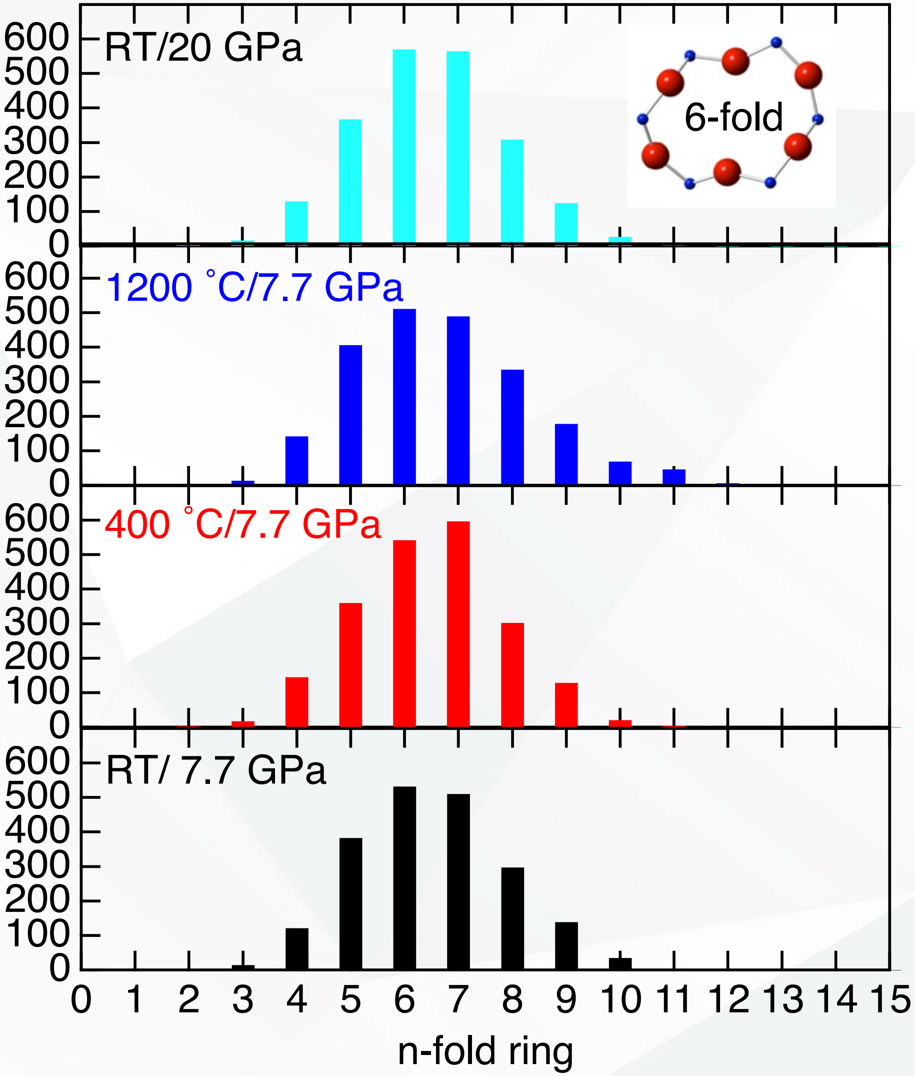
Surface based cavity



Cutoff =2.5 Å

Cavities were calculated by PyMolDyn code*

$(Si–O)_n$ ring statistics

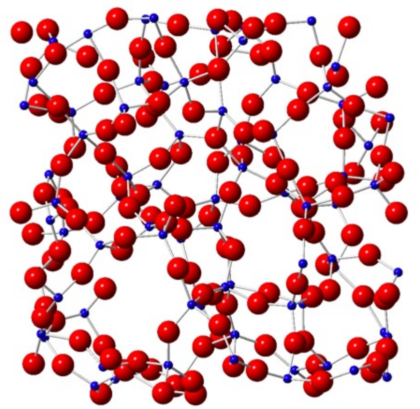


Ring size distributions show subtle changes

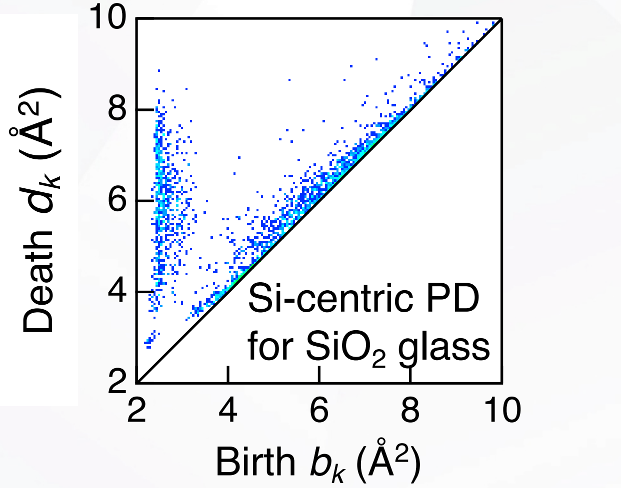
Persistent homology : Analysis of Ring Size and Shape

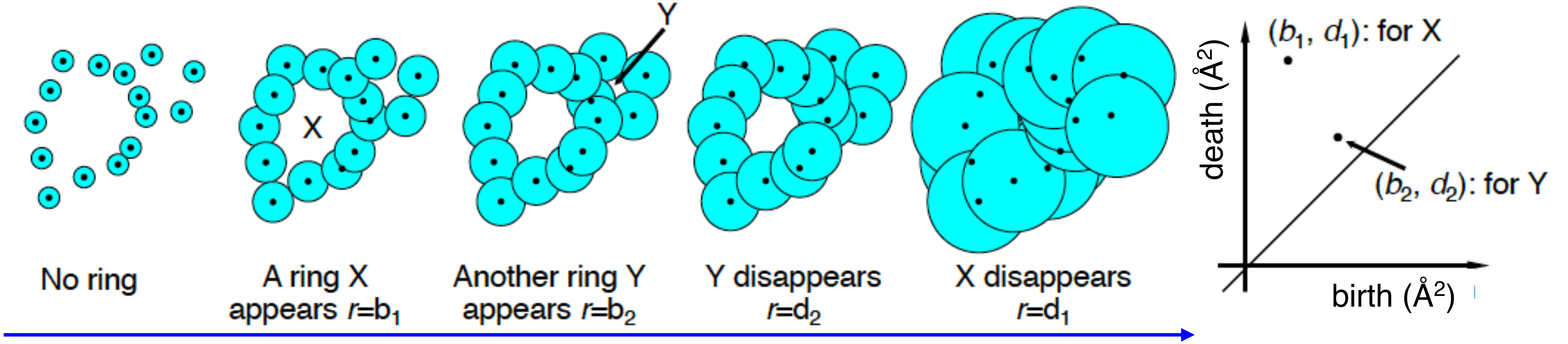
3D atomic configuration **Input** → PH_ℓ **Output** → ℓ-dimensional shape and size

Structural model of SiO_2 glass



Persistence diagram (PD)

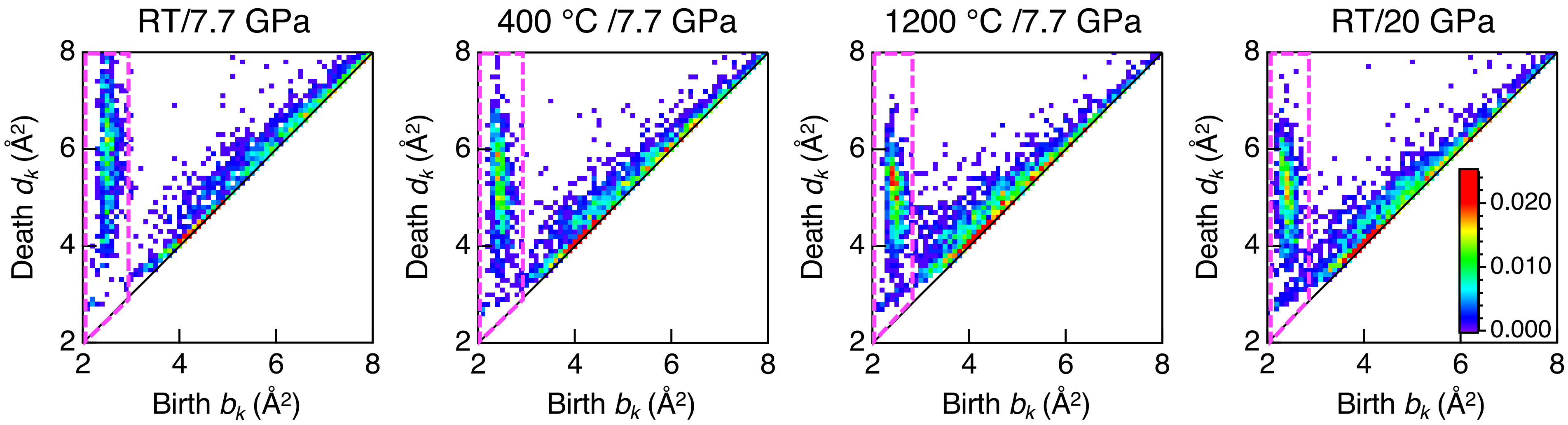


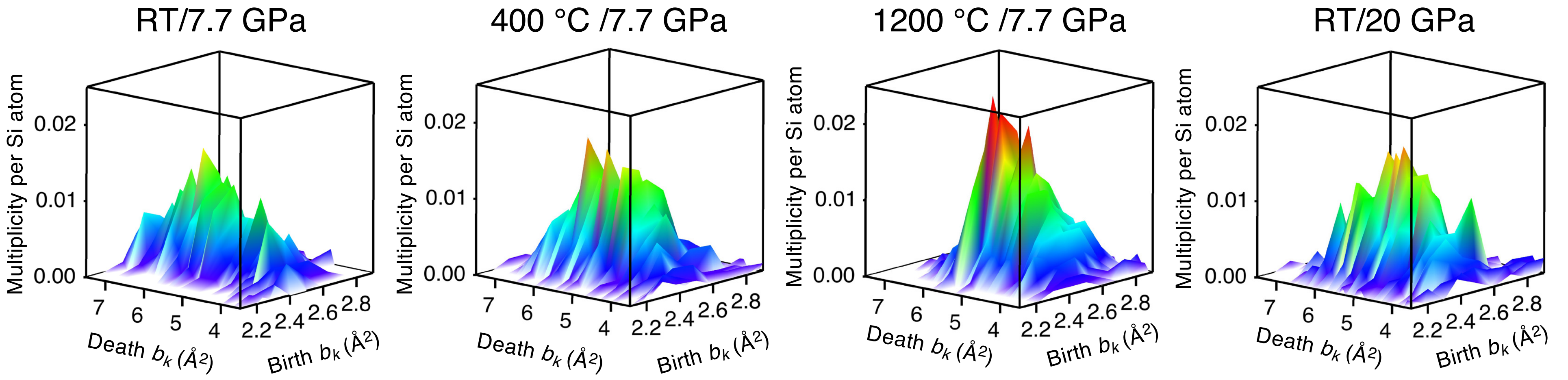


Increase the radius of sphere

* Y. Hiraoka *et al.*, *Proc. Natl. Acad. Sci.*, **113**, 7035 (2016).

Si-centric PDs for densified SiO_2 glasses





At HCG (1200 ˚C/7.7 GPa), the profiles are concentrated in the small Death (Ordering of siicon atoms)

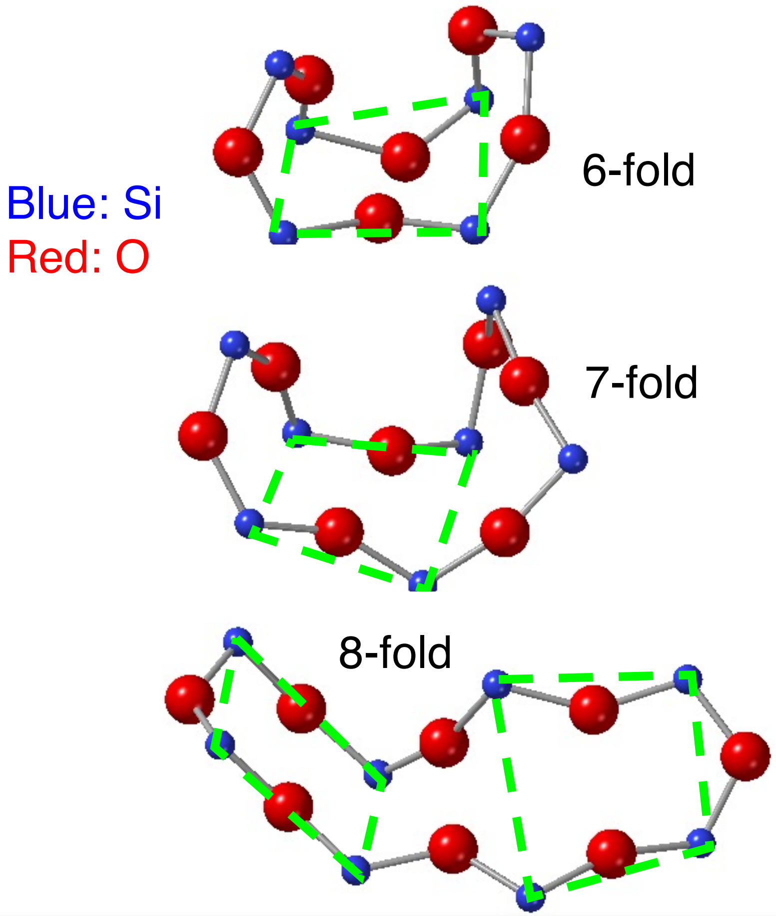
➡

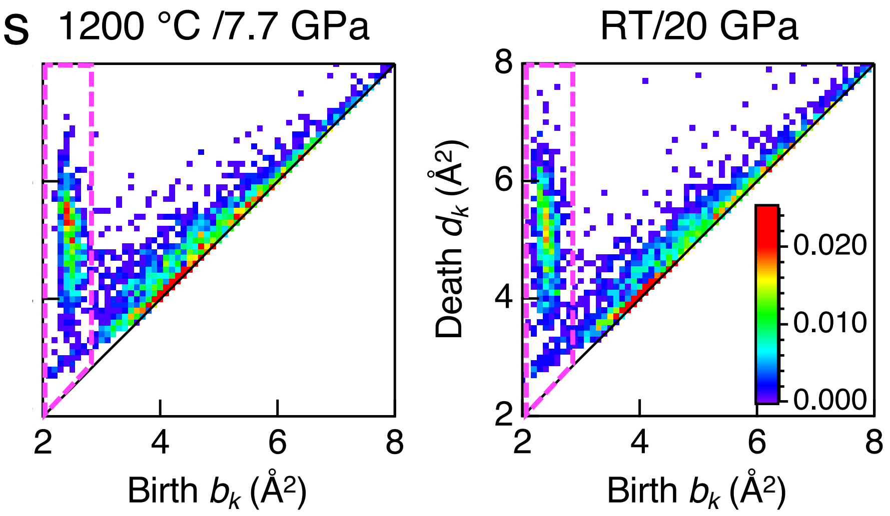
The ordering of silicon atoms stems from ring deformation

※Ring size distributions show subtle changes for densification

Si-centric PDs for densified SiO_2 glasses

Ring structures extracted from the structural model of 1200 ˚C/7.7 GPa glass

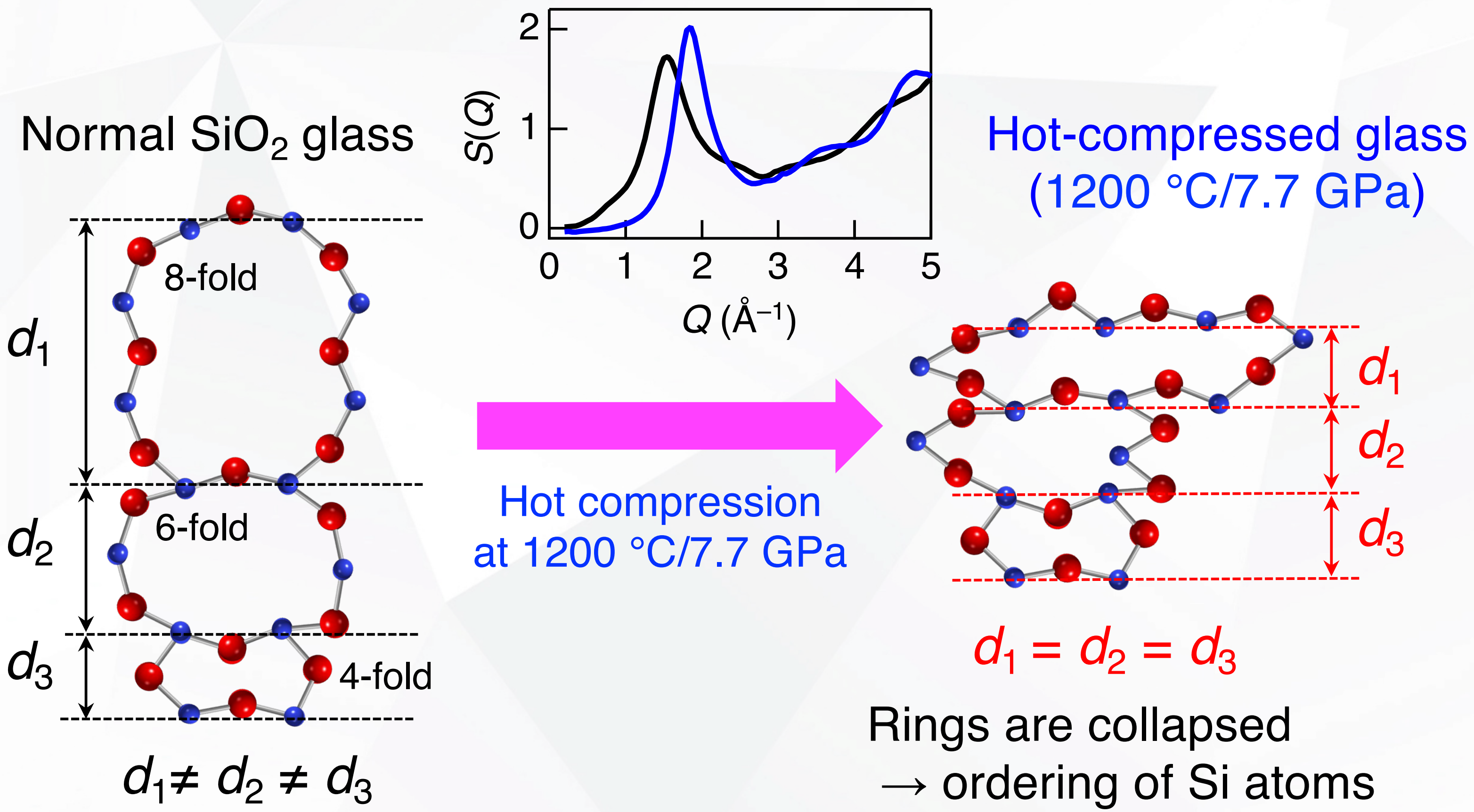




6-, 7-, and 8-fold rings in the hot-compressed glass exhibit the order of 4-fold ring as the result of deformation

Structural ordering induced by hot compression

The evolution of FSDP



Normal SiO_2 glass

$d_1 \neq d_2 \neq d_3$

Hot compression at 1200 °C/7.7 GPa

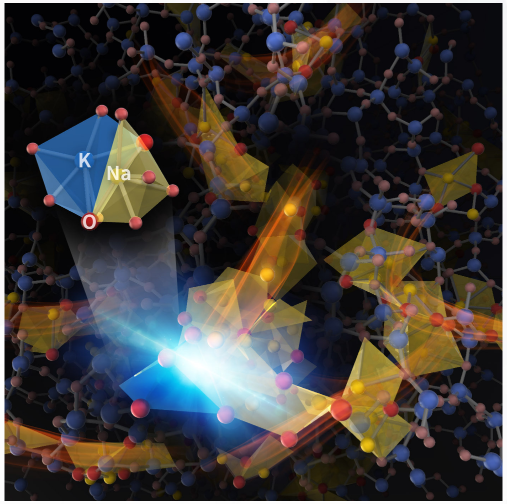
Hot-compressed glass (1200 °C/7.7 GPa)

$d_1 = d_2 = d_3$

Rings are collapsed
→ ordering of Si atoms

The distinct features in the network topology indicate that open structure of glass is collapsed, leading to ordering of Si atoms manifested by the evolution of FSDP

The origin of mixed alkali effect in silicate glass

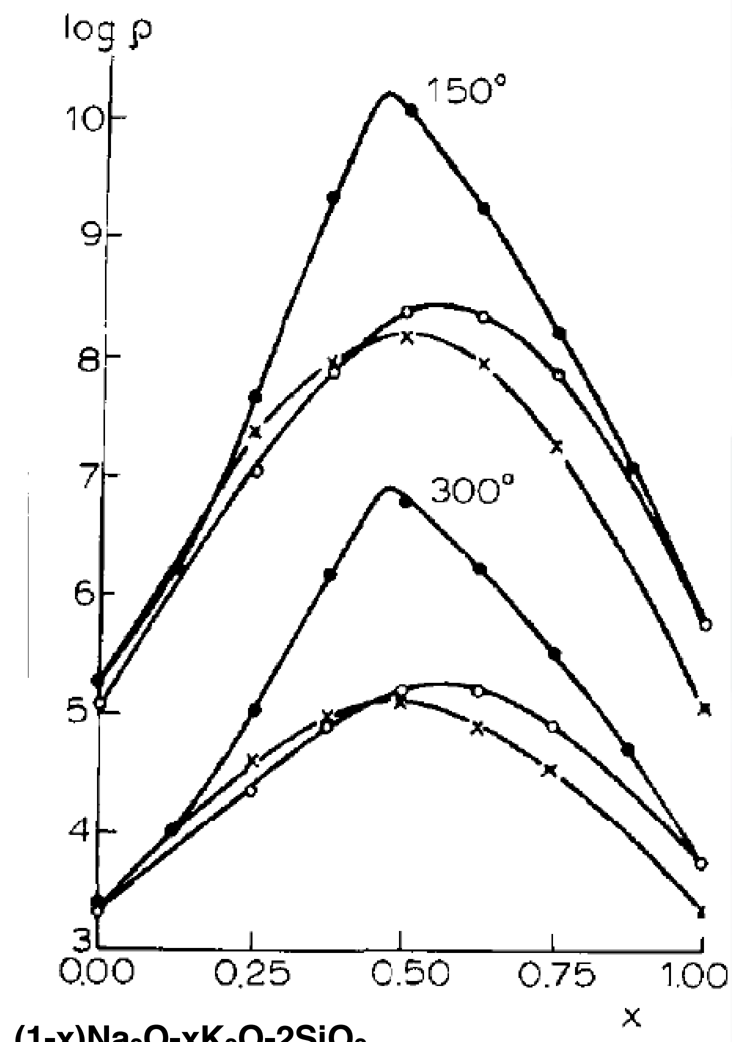


Y. Onodera *et al.*, *NPG Asia Mater.* 11, 75 (2019).
"Origin of the mixed alkali effect in silicate glass"

- ✓ Constructing three-dimensional structural models of alkali silicate glasses that reproduce quantum beam diffraction and NMR data
- ✓ Successfully extracted the structure responsible for the mixed alkali effect, which plays a crucial role in glass properties

Mixed alkali effect

Electrical resistivity
for alkali silicate glasses*



○ : $(1-x)Na_2O-xK_2O-2SiO_2$
× : $(1-x)Li_2O-xNa_2O-2SiO_2$
● : $(1-x)Li_2O-xK_2O-2SiO_2$

Electrical resistivity shows pronounced maxima in mixed alkali glasses

Mixed alkali effect

If one alkali oxide is gradually replaced by another in a series of glasses, some physical properties change in an extremely non-linear manner

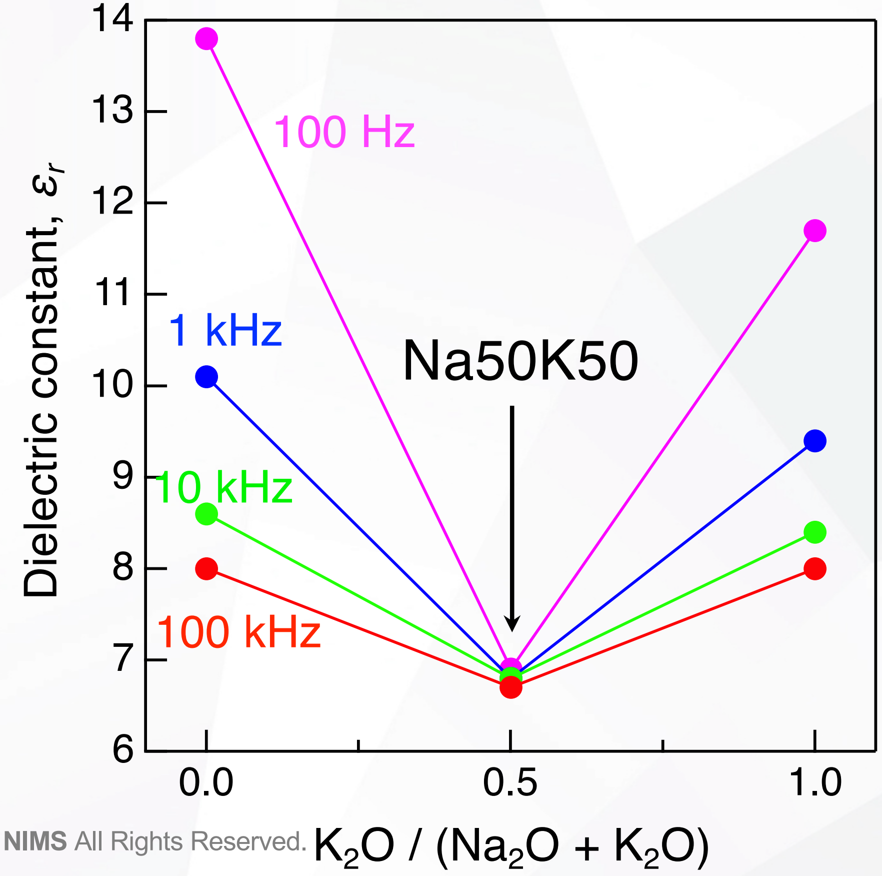
Structural origin for the mixed alkali effect
in glass is still an interesting topic in glass science

*J. O. Isard, *J. Non-Cryst Solids* **1**, 235–261 (1969).

The mixed alkali effect in alkali silicate glasses

R_2O–SiO_2 glass	Nominal composition (mol%)			Density (g/cm^3)
	Na_2O	K_2O	SiO_2	
Na100	22.7		77.3	2.429
Na50K50	11.3	11.3	77.3	2.439
K100		22.7	77.3	2.404

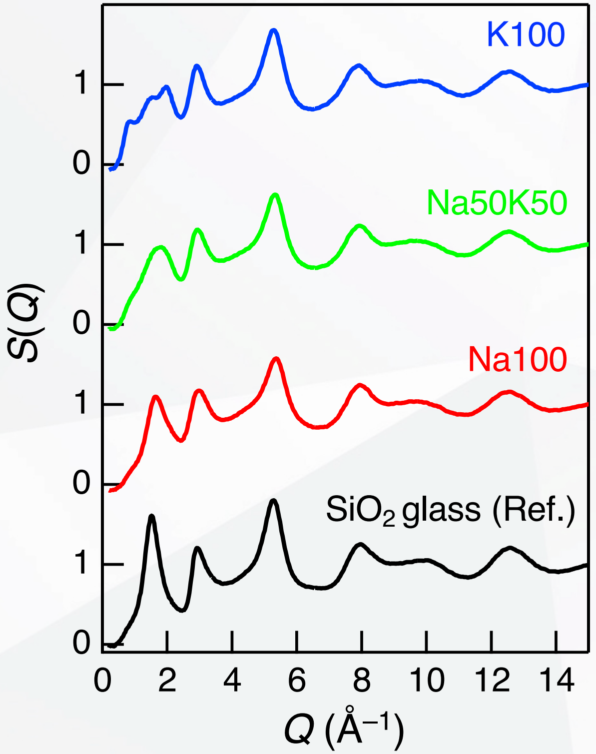
Dielectric constants, ε_r, for $22.7R_2O$–$77.3SiO_2$ glass

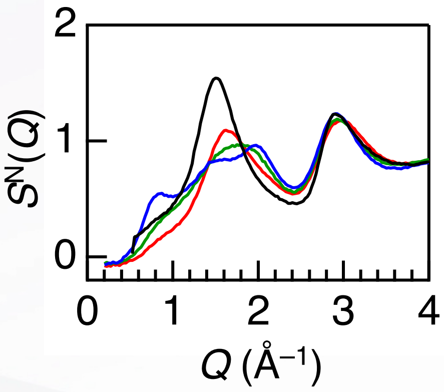


The mixed alkali effect

ε_r for R_2O–SiO_2 glass shows:

- ✓ Non-linear trend as a function of K_2O amount
- ✓ Minimum value in Na50K50 glass (Ionic migration was inhibited by alkali mixing)





The addition of alkali causes complex changes in FSDP (intermediate-range structure)

Structure modelling (RMC–MD)

Number of particles: 3300
(alkali atoms: 500, Si: 850, O: 1950)

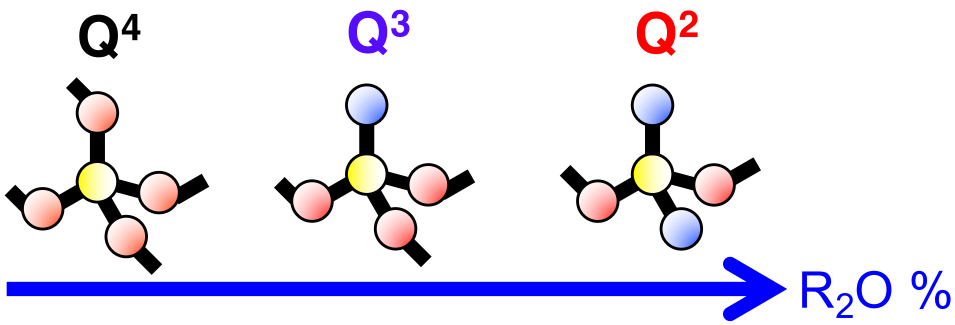
Experimental dataset:

Neutron structure factor, $S^{N}(Q)$ (NOVA/J-PARC)
(Coherent scattering length,
b_c: O > Si> K ≒ Na)

X-ray structure factor, $S^{X}(Q)$ (BL04B2/SPring-8)
(Atomic form factors,
$f(Q)$: K > Si> Na >O)

NMR*
(Ratio of Q^n units)

Yellow : Si
Red : Bridging O (BO)
Blue : Non-bridging O (NBO)



*Maekawa *et al.*, *J. Non-Cryst. Solids* **127,** 53 (1991).
A. Pedone *et al.*, *J. Phys. Chem. B* **110, 11780 (2006).

Hard sphere Monte Carlo (HSMC) simulations
to reproduce Q^n by NMR

↓

RMC (RMC++)
to fit $S^{N}(Q)$ & $S^{X}(Q)$
with geometrical constraints for Q^n

↓

MD**
to optimize configurations

↓

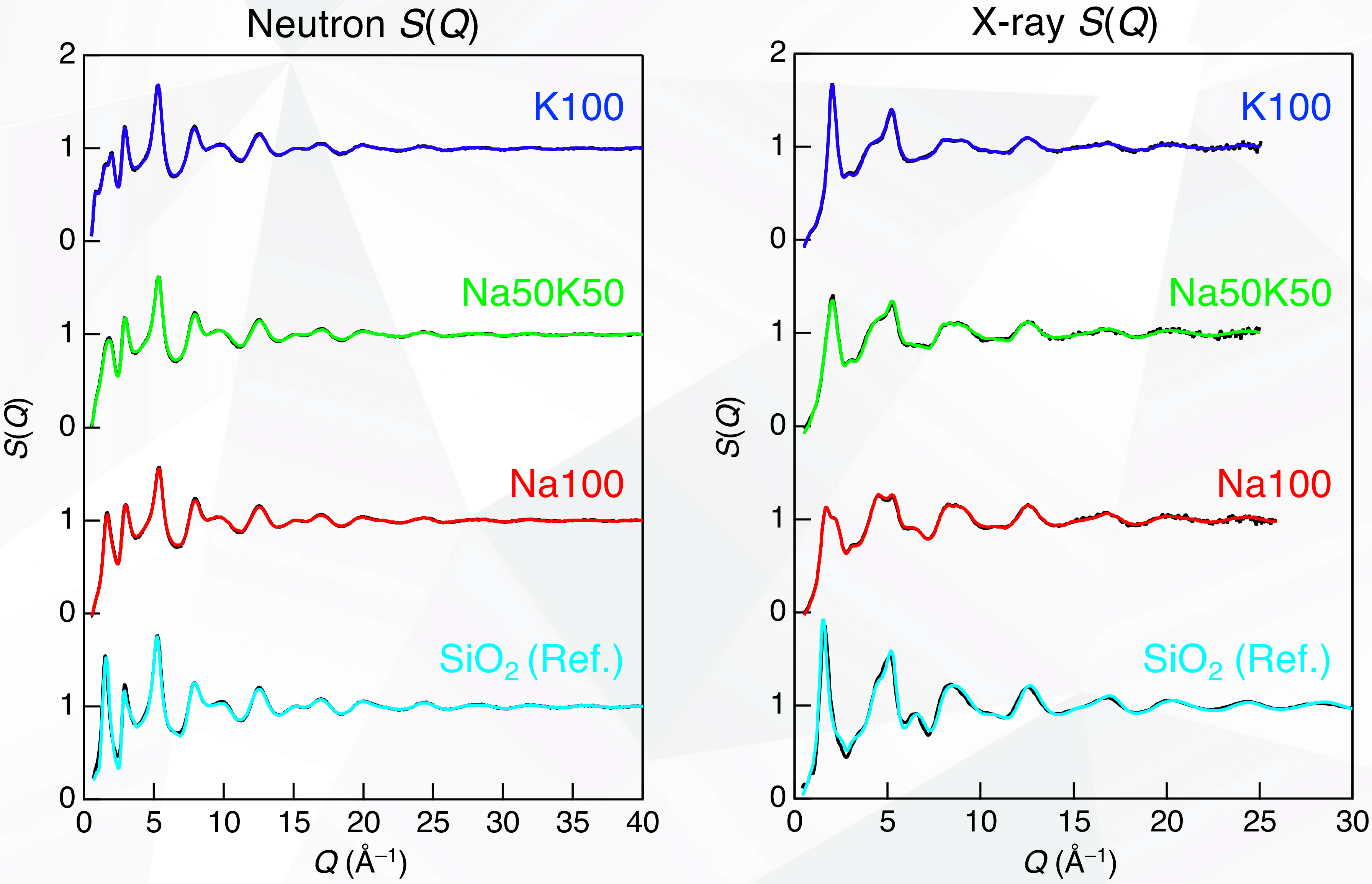
RMC (RMC++)
to refine the configurations with constraints for Q^n, Si–O coordination number, O–Si–O bond angle, partial $g(r)$s within the 1st coordination shell

↓

Final RMC–MD models

RMC-MD simulations

Black: experimental data
Red: RMC-MD (Na100)
Green: RMC-MD (Na50K50)
Blue: RMC-MD(K100)
Cyan: RMC-MD (SiO_2)



3D structure models of silicate glasses that reproduce experimental data were successfully constructed

Structure modelling (RMC–MD)

Comparison of Q^n distributions between NMR and RMC–MD model

		Q^n units				
		Q^4	Q^3	Q^2	Q^1	Q^0
Na100	**NMR***	**42.7%**	**55.8%**	**1.5%**	**-**	**-**
	RMC–MD	**43.4%**	**54.4%**	**2.2%**	**0%**	**0%**
	RMC without NMR	**49.1%**	**43.8%**	**6.5%**	**0.7%**	**0%**
Na50K50	**NMR***	**42.4%**	**56.5%**	**1.2%**	**-**	**-**
	RMC–MD	**42.8%**	**54.6%**	**2.5%**	**0%**	**0.1%**
	RMC without NMR	**49.9%**	**41.6%**	**7.6%**	**0.7%**	**0.1%**
K100	**NMR***	**42.0%**	**57.2%**	**0.8%**	**-**	**-**
	RMC–MD	**43.6%**	**53.2%**	**3.2%**	**0%**	**0%**
	RMC without NMR	**52.9%**	**36.1%**	**10.1%**	**0.8%**	**0%**

RMC–MD models successfully reproduced Q^n distributions on the basis of the results of NMR

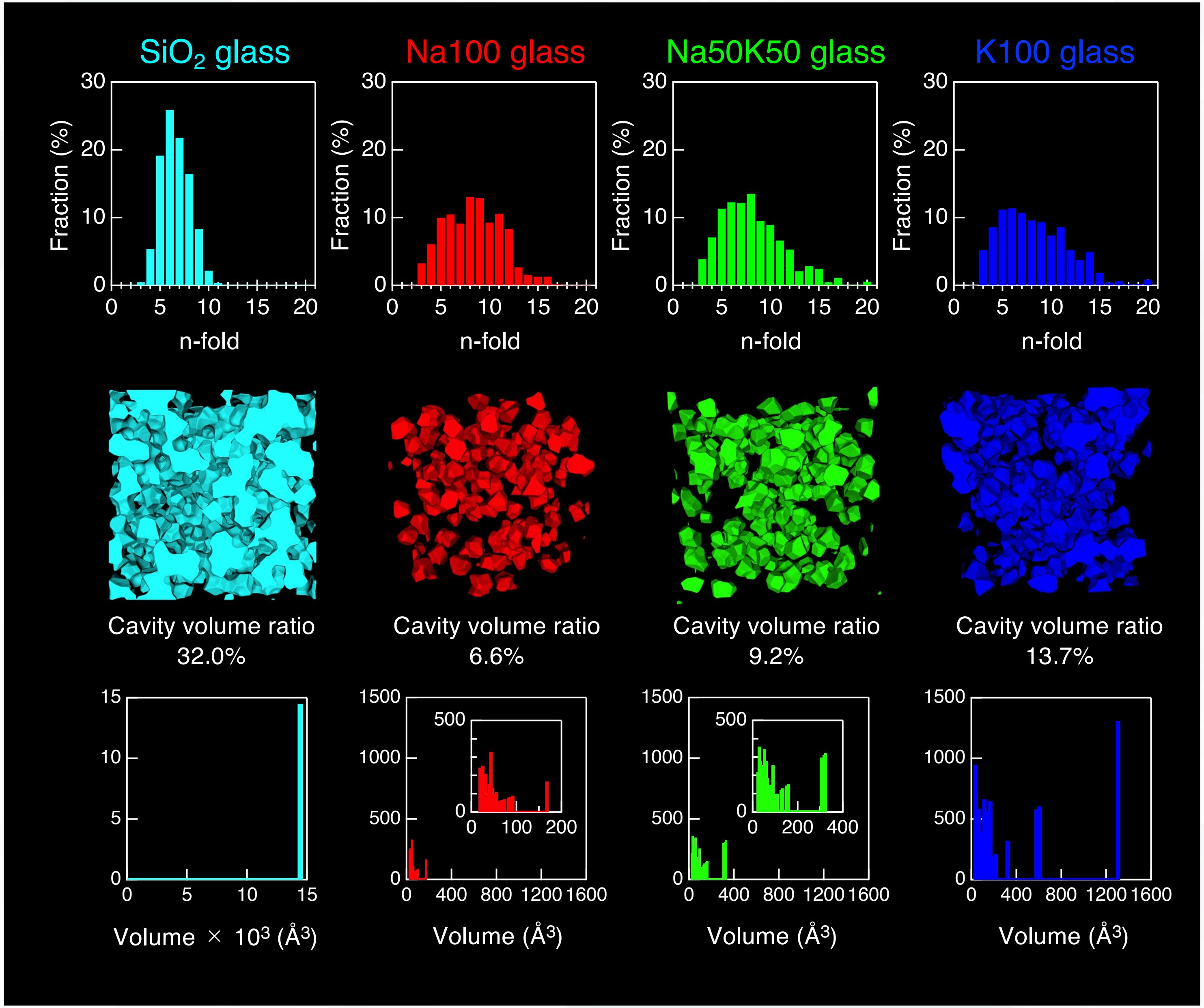
*Maekawa *et al.*, *J. Non-Cryst. Solids* **127**, 53 (1991).

Ring statistics and cavities in silicate glasses

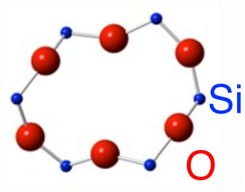
$(\text{Si-O})_n$ ring statistics

Visualized Cavities

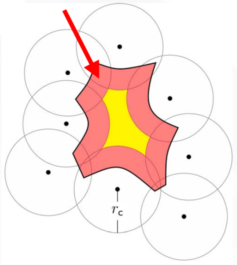
Cavity size distributions

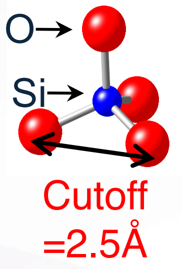


6-fold ring



Surface based cavity





Na–O and K–O coordination number analysis

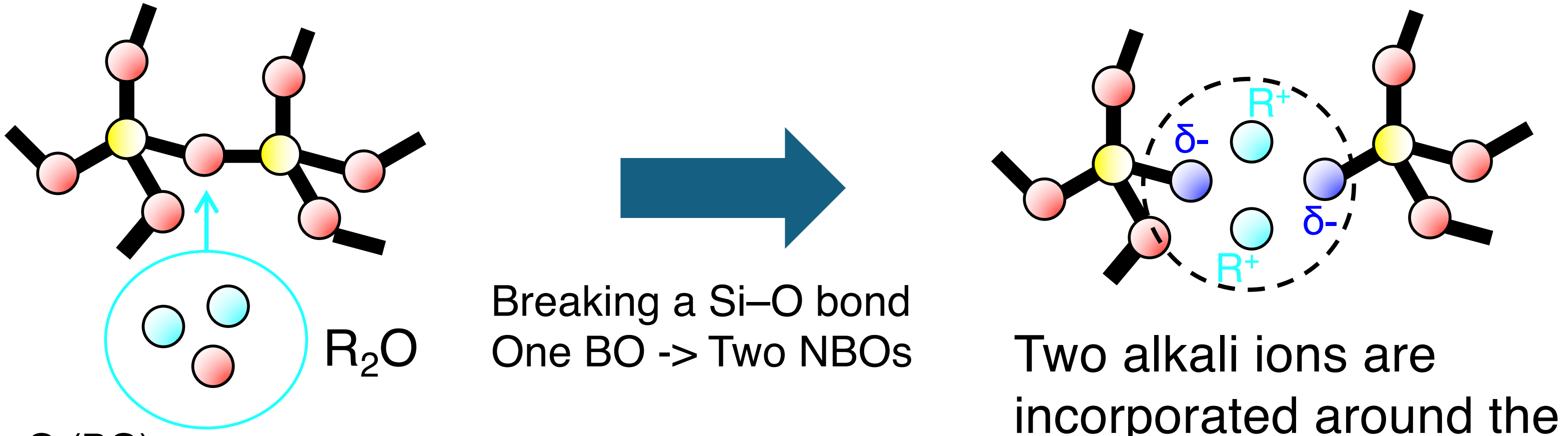
Alkali–oxygen coordination numbers were calculated from RMC–MD models

Glass	Na100	Na50K50	K100
$N_{\text{Na–O}}$	**4.2**	**4.1**	**-**
$N_{\text{Na–BO}}$	**2.1**	**2.0**	**-**
$N_{\text{Na–NBO}}$	**2.1**	**2.1**	**-**
$N_{\text{K–O}}$	**-**	**5.2**	**4.4**
$N_{\text{K–BO}}$	**-**	**2.9**	**2.3**
$N_{\text{K–NBO}}$	**-**	**2.3**	**2.1**

First coordination distance:
Na–O: 3.0 Å, K–O: 3.3 Å

The alkali–NBO coordination number is approximately 2

$N_{\text{K–BO}}$ in Na50K50 glass is larger than that in K100



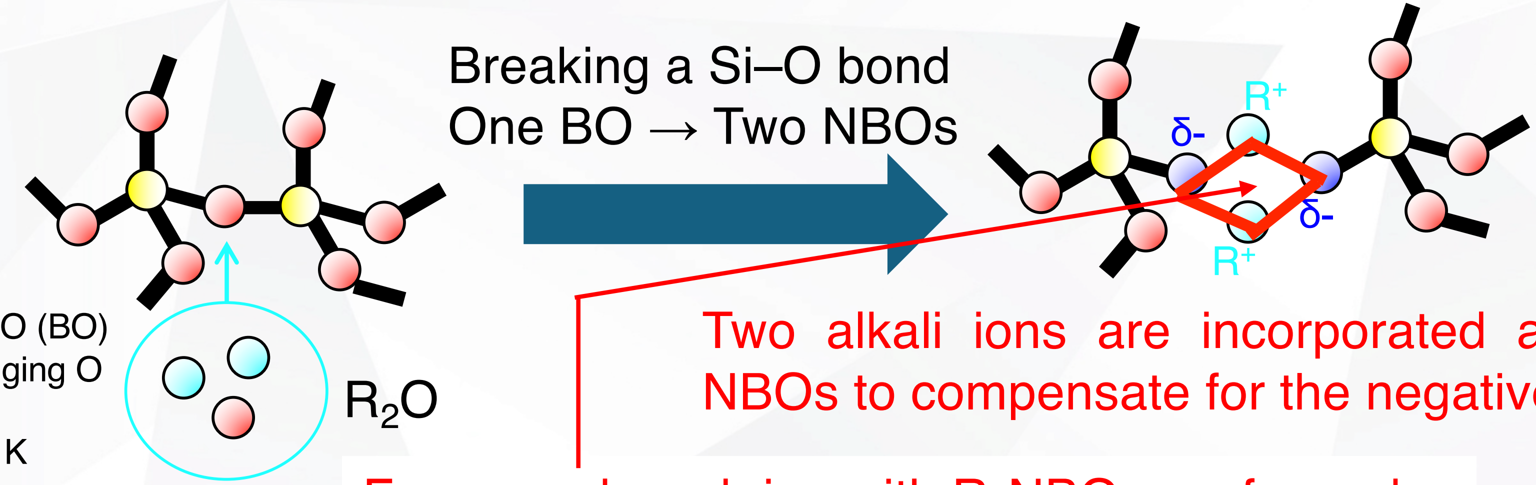
Breaking a Si–O bond
One BO -> Two NBOs

Two alkali ions are incorporated around the NBOs to compensate for the negative charges of the NBOs

Yellow：Si
Red：Bridging O (BO)
Blue：Non-bridging O (NBO)
Cyan：R＝Na, K

Extraction of the origin of mixed alkali effect

The SiO_4 network modification by Introducing the alkali oxide (R_2O)



Breaking a Si–O bond
One BO → Two NBOs

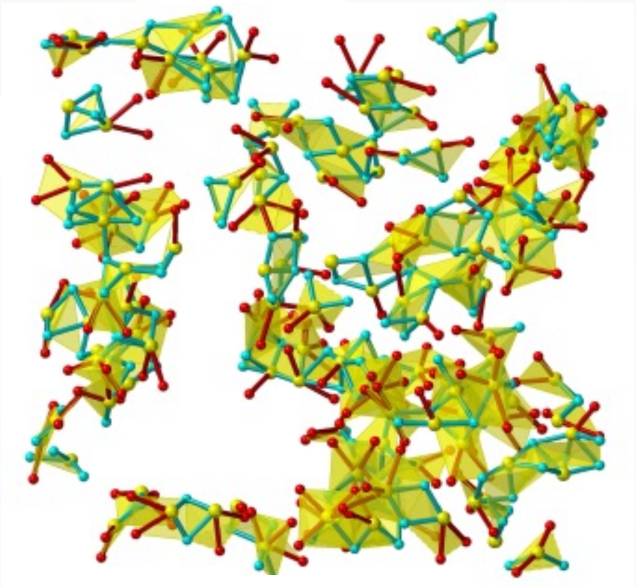
Yellow: Si
Red: Bridging O (BO)
Blue: Non-bridging O (NBO)
Cyan: R=Na, K

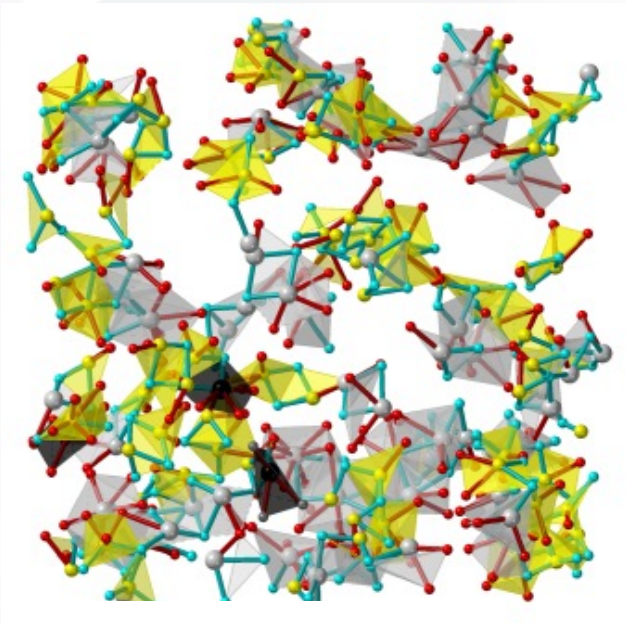
R_2O

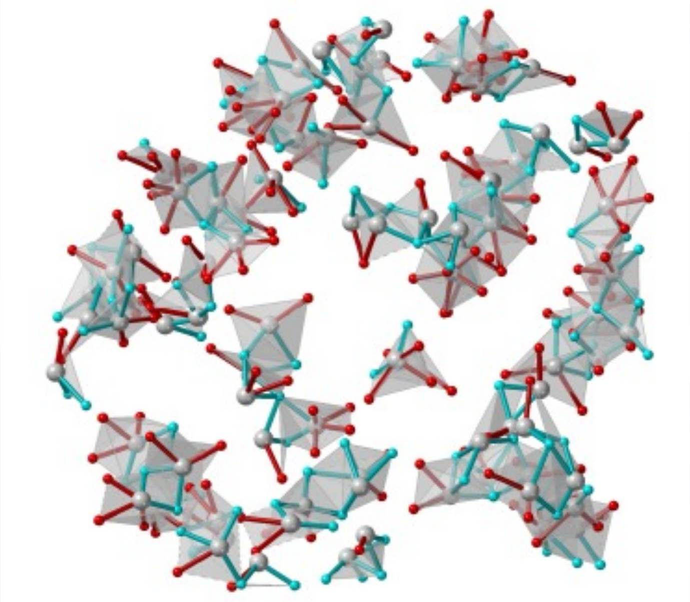
Two alkali ions are incorporated around the NBOs to compensate for the negative charges

Four-membered ring with R_2NBO_2 are formed

Yellow: Na, Cyan: K, Red: BO, Cyan: NBO


Na100 glass

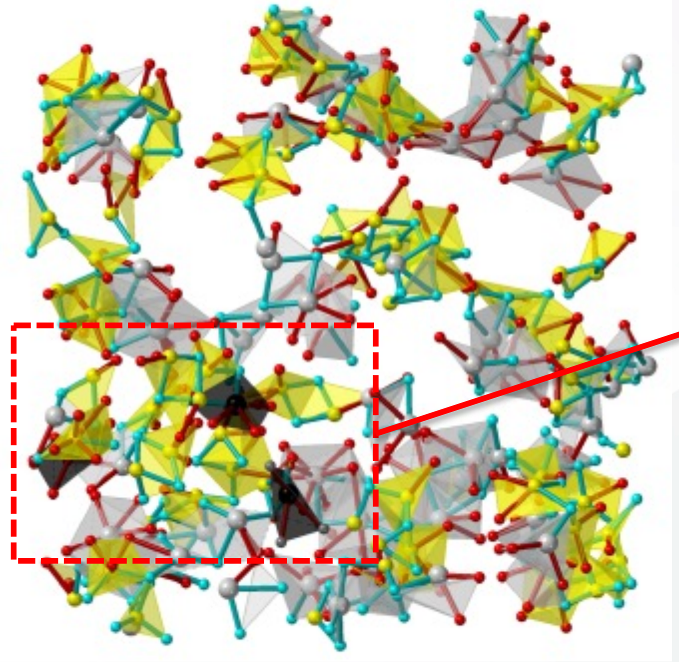

Na50K50 glass


K100 glass

Extracted structures stands for the mixed alkali effect in Na50K50 glass

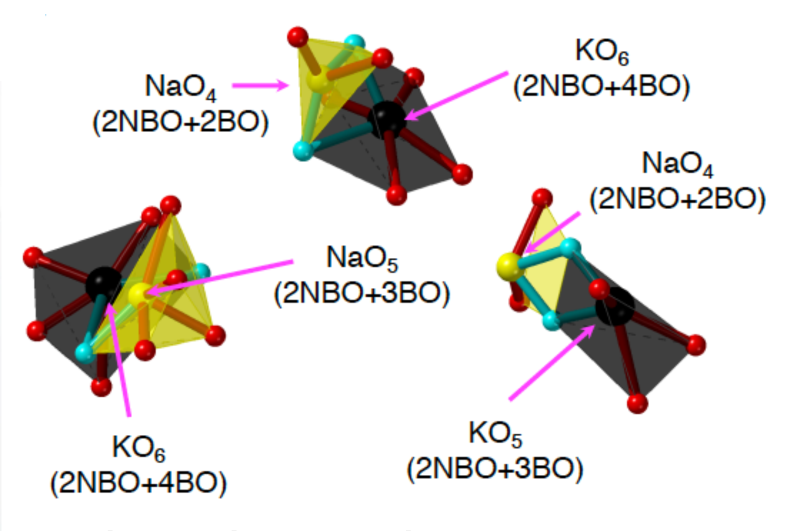
Extracted structures surrounding alkali in Na50K50glass

Na50K50 glass



Yellow: Na
Grey: K
Red: BO
Cyan: NBO

Typical bottle neck structure



Edge-sharing between $(Na–O)_x$ and $(K–O)_x$ polyhedra

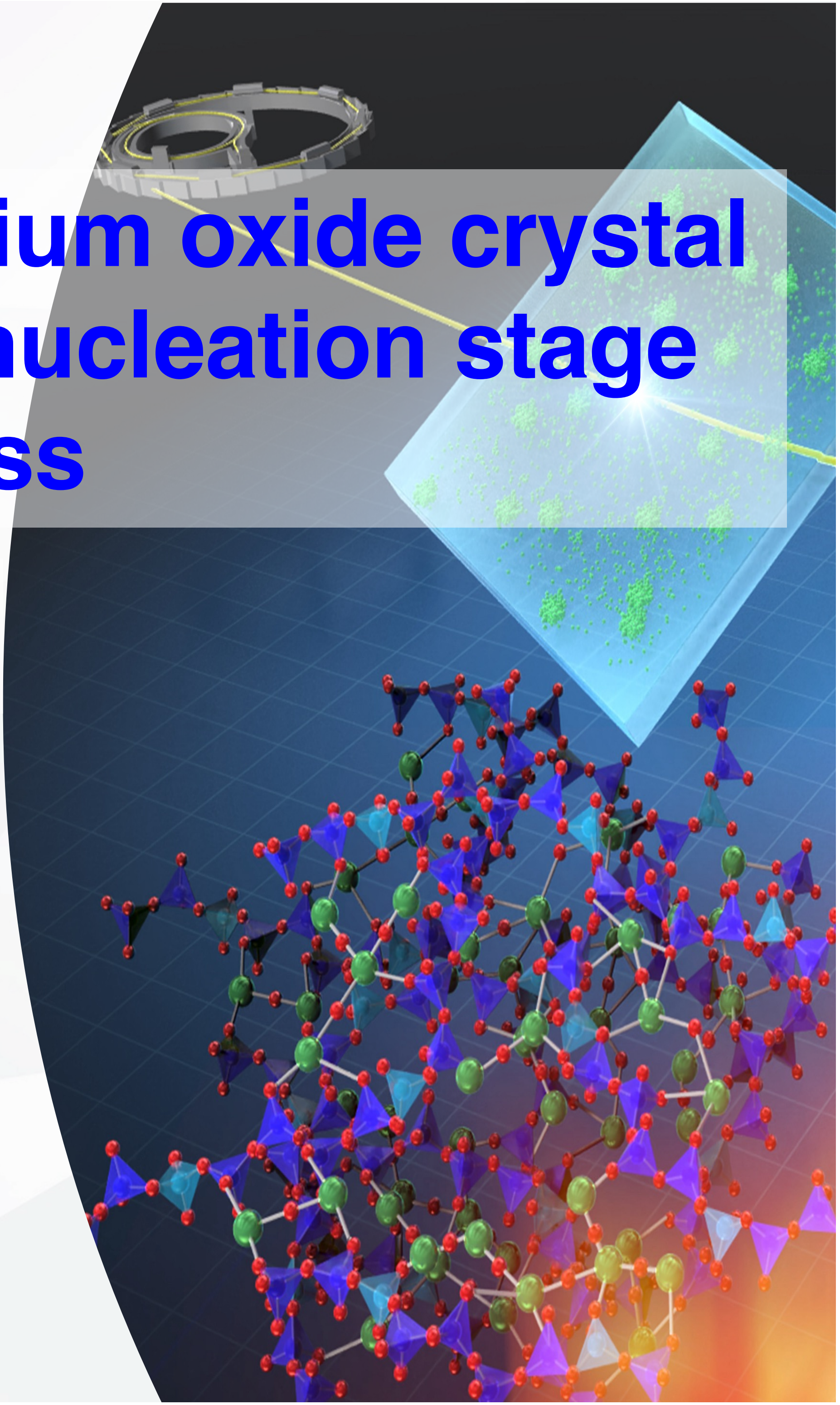
K ion is trapped by a higher number of BO atoms in Na50K50 glass

The local environment of K ions in the highly coordinated K–O polyhedra (black) is significantly different from that of Na ions in the four coordinated Na–O polyhedra

The specific correlations between the different alkali ions profoundly inhibits the ionic migration in Na50K50 glass

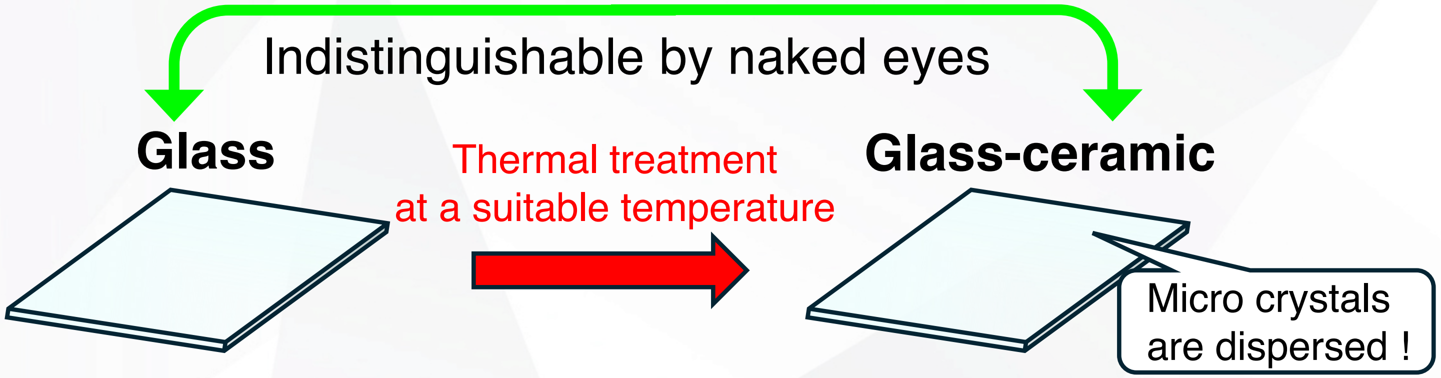
Formation of a zirconium oxide crystal nucleus in the initial nucleation stage in aluminosilicate glass

Y. Onodera *et al.*,
NPG Asia Mater., 16, 22 (2024).



Introduction: Glass-ceramics

Glass-ceramics are composed precipitated crystals and a glass matrix



Indistinguishable by naked eyes

Glass

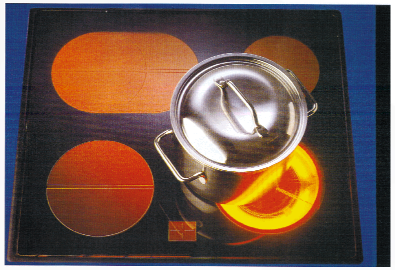
Thermal treatment
at a suitable temperature

Glass-ceramic

Micro crystals
are dispersed !

- ☺ Transparent
- ☺ Insulator
- ☺ High mechanical strength
- ☹ Fragile
- ☹ Susceptible to rapid temperature change

- ☺ Transparent
- ☺ Insulator
- ☺ High mechanical strength
- ☺ Strong (compared with glass)
- ☺ Thermal shock resistance



E. D. Zanotto,
Am. Ceram. Soc. Bull.,
89, 19 (2010).

Zirconium oxide (ZrO_2)-doped aluminosilicate systems
: the most important commercial glass-ceramics

The Zr^{4+} environment in the early stage of nucleation was not well understood

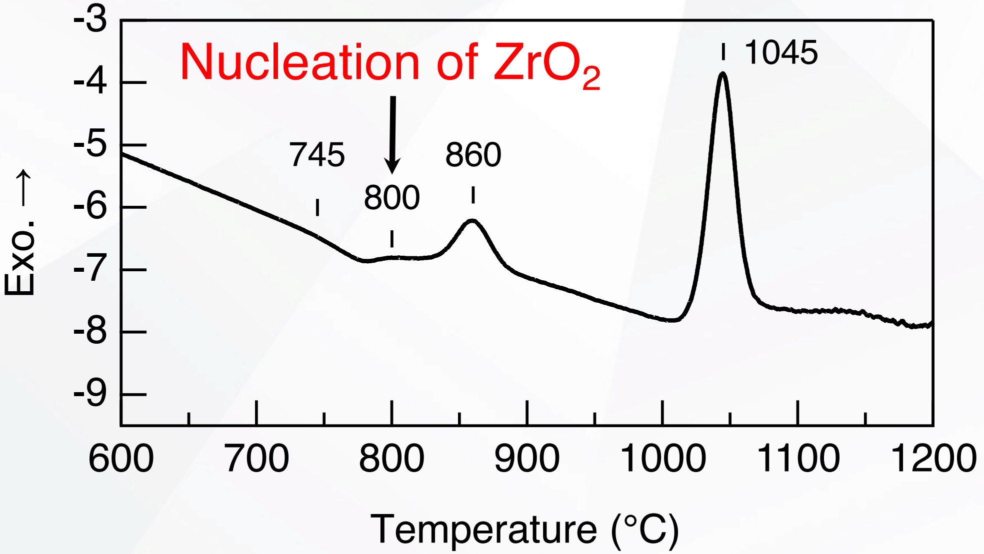
Aim of this study

Investigating a ZrO_2 crystal nucleus in the initial nucleation stage in aluminosilicate glass

Pristine glass composition

component	mol%
SiO_2	70.7
Al_2O_3	14.3
P_2O_5	0.7
ZrO_2	2.9
Li_2O	9.3
Na_2O	2.1
Total	100.0

Differential scanning calorimetry (DSC) curve



✓Glass transition temperature: 745 °C

✓Three exothermic peaks: 800, 860, 1045 °C

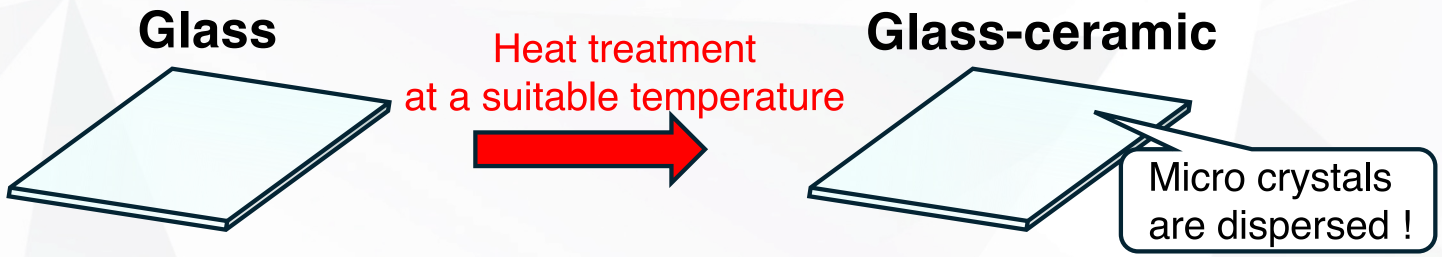
The pristine glass was annealed at 770 °C for various durations (1–48 h)

⇩

A series of glass-ceramic samples at different nucleation stages

Aim of this study

Zr^{4+} environment in the initial nucleation stage??



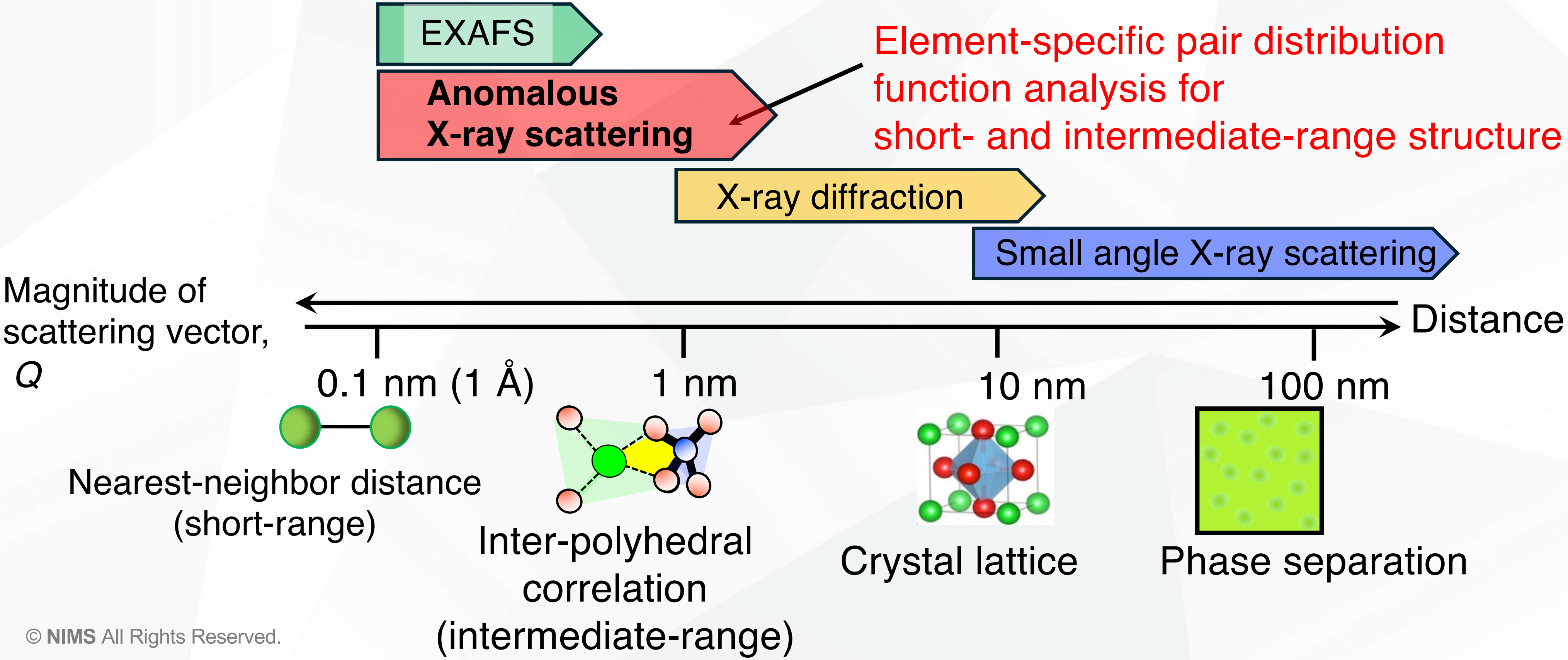
Glass

Heat treatment
at a suitable temperature

Glass-ceramic

Micro crystals
are dispersed !

X-ray multiscale structural analysis



EXAFS

**Anomalous
X-ray scattering**

Element-specific pair distribution
function analysis for
short- and intermediate-range structure

X-ray diffraction

Small angle X-ray scattering

Magnitude of
scattering vector,
Q

Distance

Nearest-neighbor distance
(short-range)

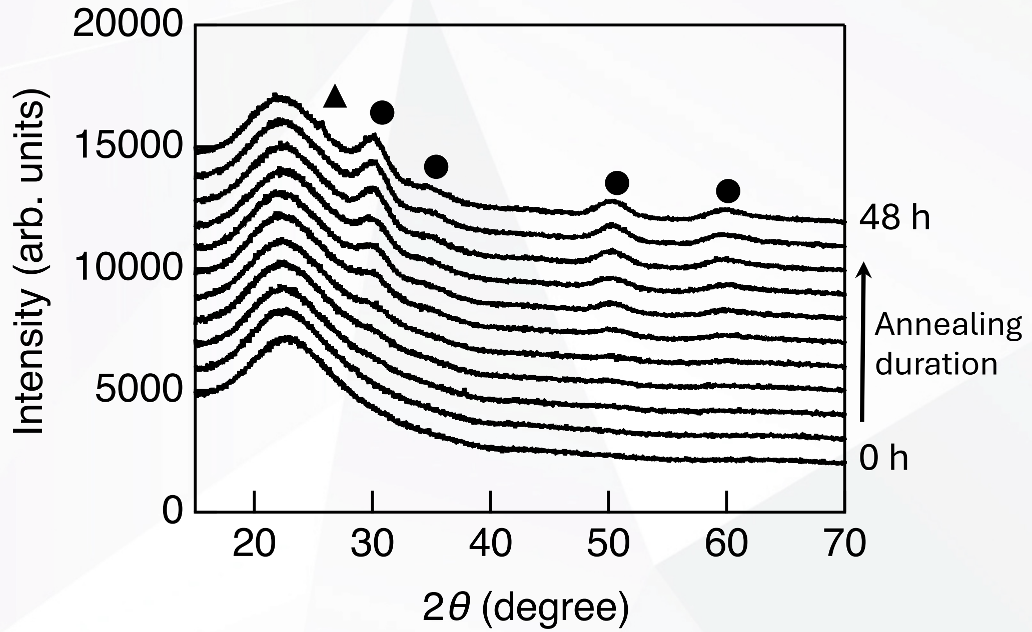
Inter-polyhedral
correlation
(intermediate-range)

Crystal lattice

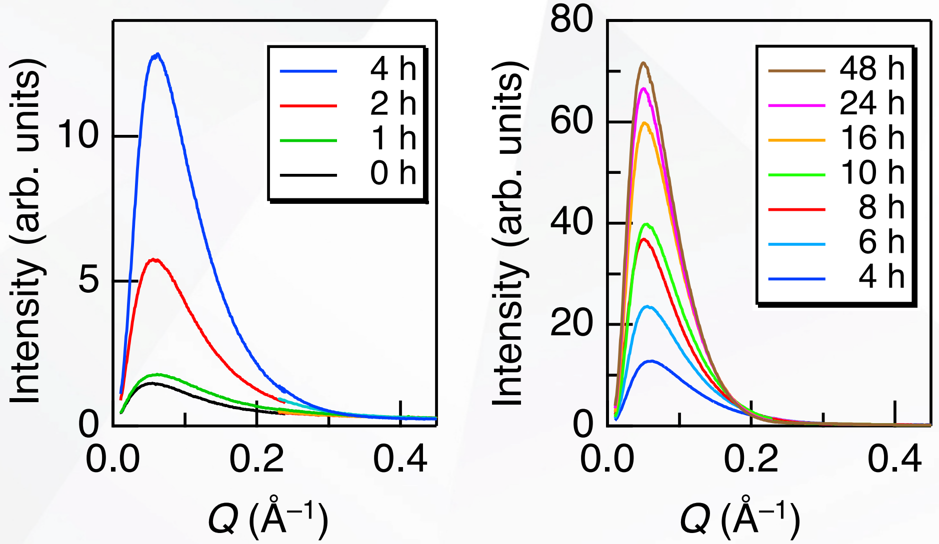
Phase separation

X-ray diffraction and small angle X-ray scattering – nanoscale structure analysis

In-house X-ray diffraction (XRD) patterns



Small angle X-ray scattering (SAXS) profiles



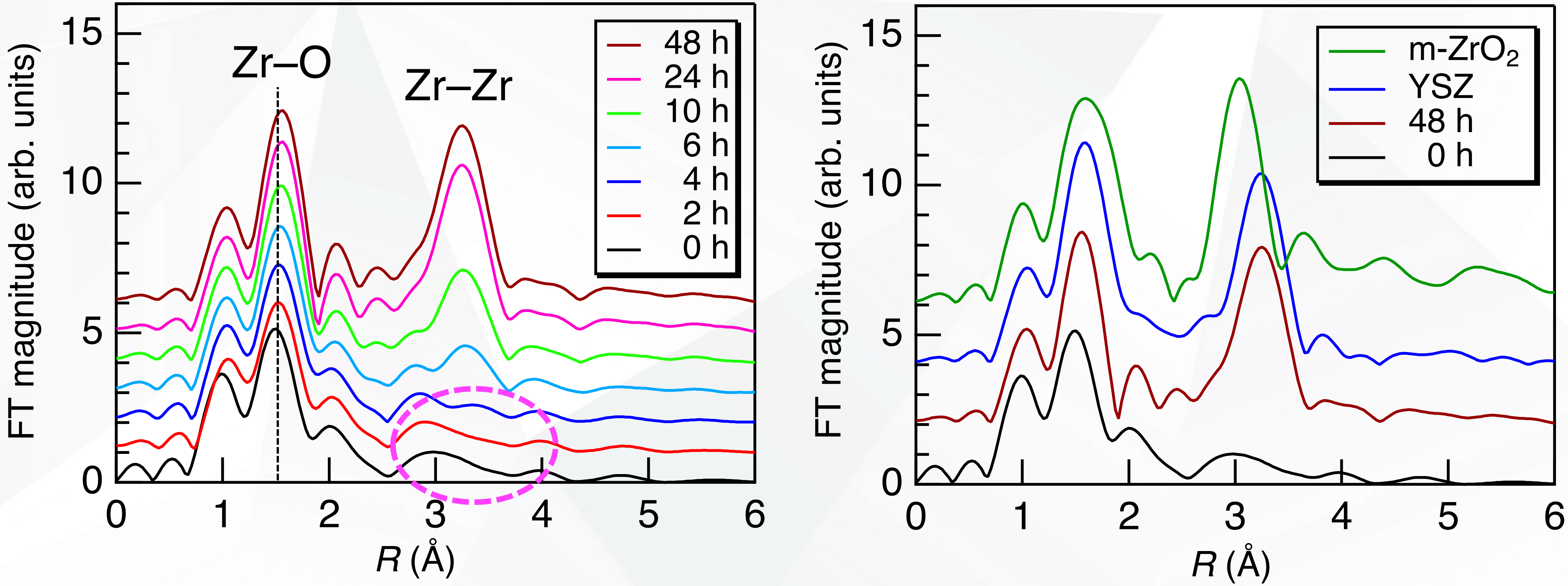
Nanoscale structural change by annealing:

- ✓ Subtle XRD peaks assigned to cubic or tetragonal ZrO_2 ($\geqq$ 4 hours)
- ✓ The size of the ZrO_2 crystallites was almost unchanged
  (only the number of the ZrO_2 crystallites increased)
- ✓ Contrast in Zr concentration between Zr-poor and Zr-rich regions increased
  (the pristine glass has an inherent inhomogeneous structure)
- ✓ The distance between Zr-rich and Zr-poor regions was unchanged

EXAFS data – short-range structure analysis

Fourier transform of k^3-weighted EXAFS functions

YSZ: yttria-stabilized ZrO_2



✓The Zr–O coordination number gradually increased over 4 h of annealing
→ reached approximately 7 after 48 h

✓ The EXAFS spectra for the 48-h-annealed and YSZ samples were almost the same
→ Cubic or tetragonal ZrO_2 microcrystalline phase (not monoclinic)

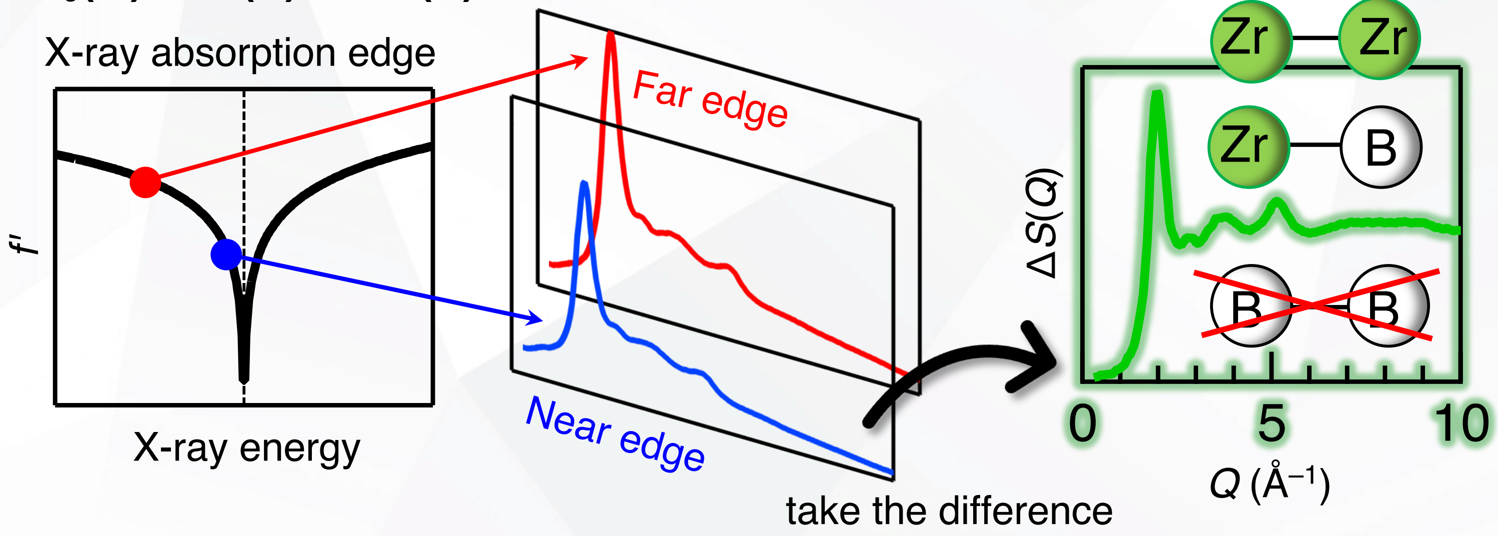
Observing atomic correlations beyond the first coordination shell in glass-ceramics during the early stage of nucleation was difficult

Anomalous X-ray scattering (AXS)* experiment

*Y. Waseda. Springer-Verlag, Heidelberg (1984).

Anomalous variations in the X-ray atomic form factor of a specific element close to the absorption edge due to the influence of the anomalous dispersion term, f'

$$f(Q, E) = f_0(Q) + f'(E) + if''(E)$$



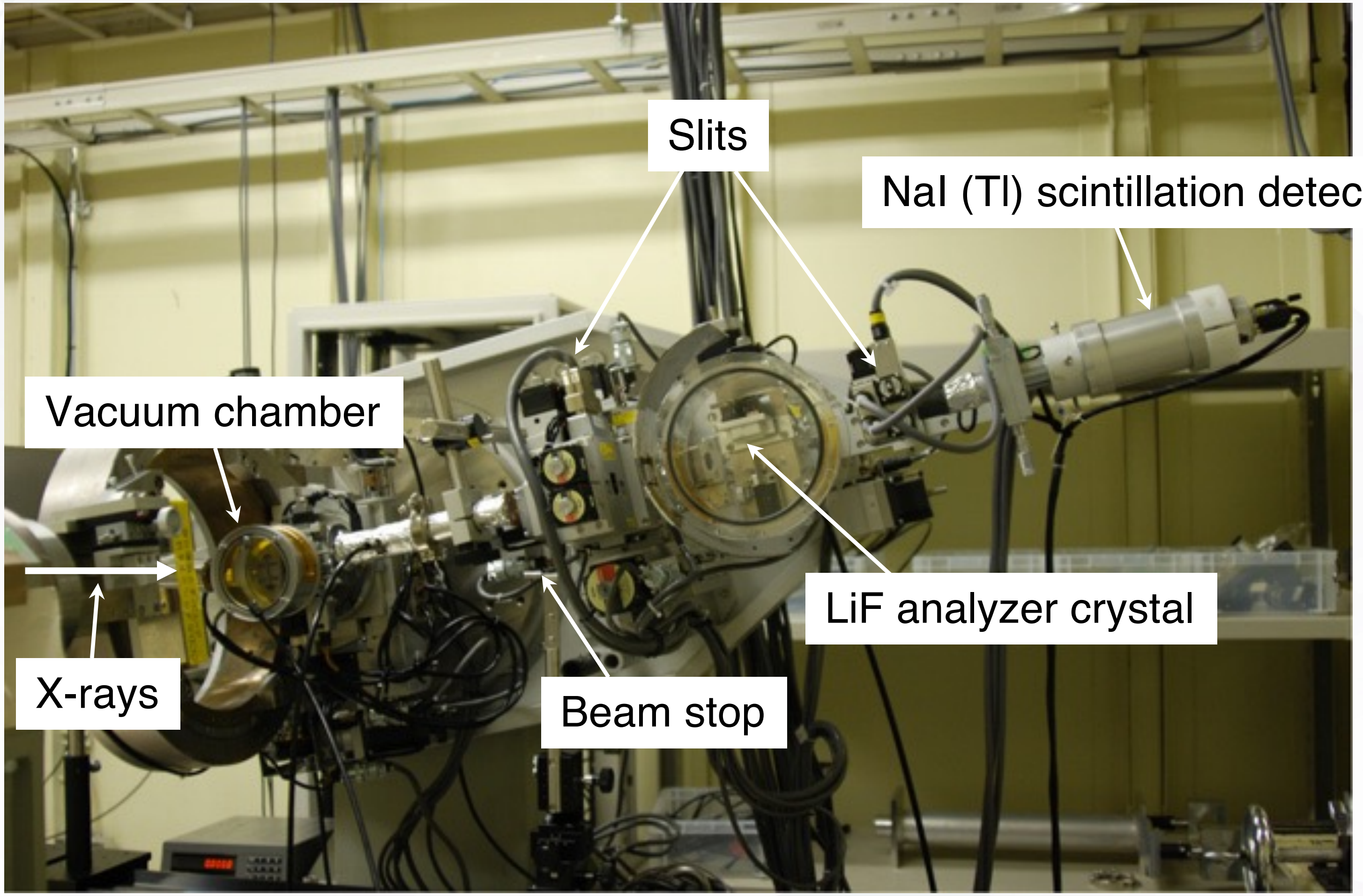
Only structural information related to specific element are obtained by taking the difference between X-ray scattering patterns measured at far edge and near edge

AXS provides element-specific pair distribution functions (PDF) including structural information beyond the nearest-neighbor distance

$$\Delta_{\mathrm{Zr}}S(Q) \\ = 0.033S_{\mathrm{ZrZr}}(Q) + 0.312S_{\mathrm{ZrSi}}(Q) + 0.117S_{\mathrm{ZrAl}}(Q) + 0.018S_{\mathrm{ZrLi}}(Q) + 0.015S_{\mathrm{ZrNa}}(Q) + 0.521S_{\mathrm{ZrO}}(Q)$$

AXS spectrometer installed at BL13XU/SPring-8*

SPring-8
http://www.spring8.or.jp

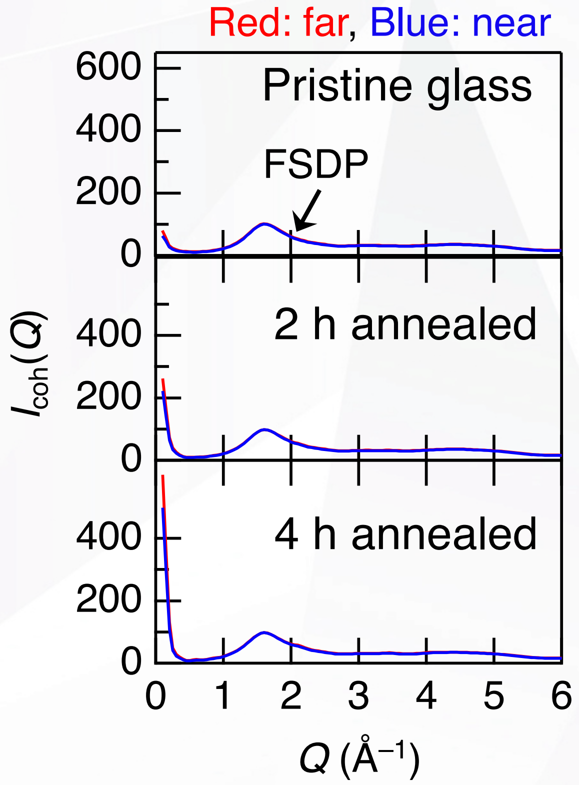


AXS measurements at two incident X-ray energies:
17.81 keV (Zr far edge, E_{far})
17.99 keV (Zr near edge, E_{near})

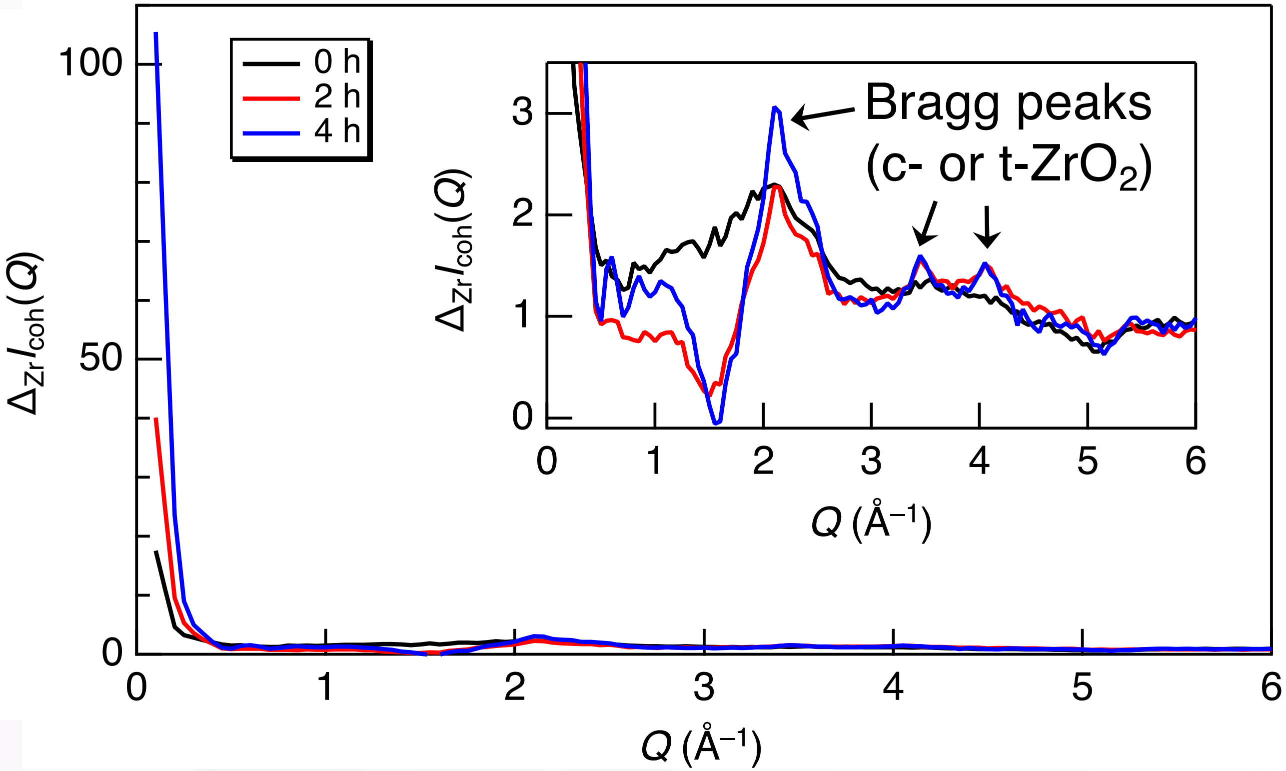
*K. Ohara *et al.*, J. Phys.: Condens. Mater, **33**, 383001 (2021).

AXS data (Zr K-edge)
– short- and intermediate-range structure analysis

Total X-ray scattering intensities



Differential intensities $\Delta_{Zr}I_{coh}(Q)$

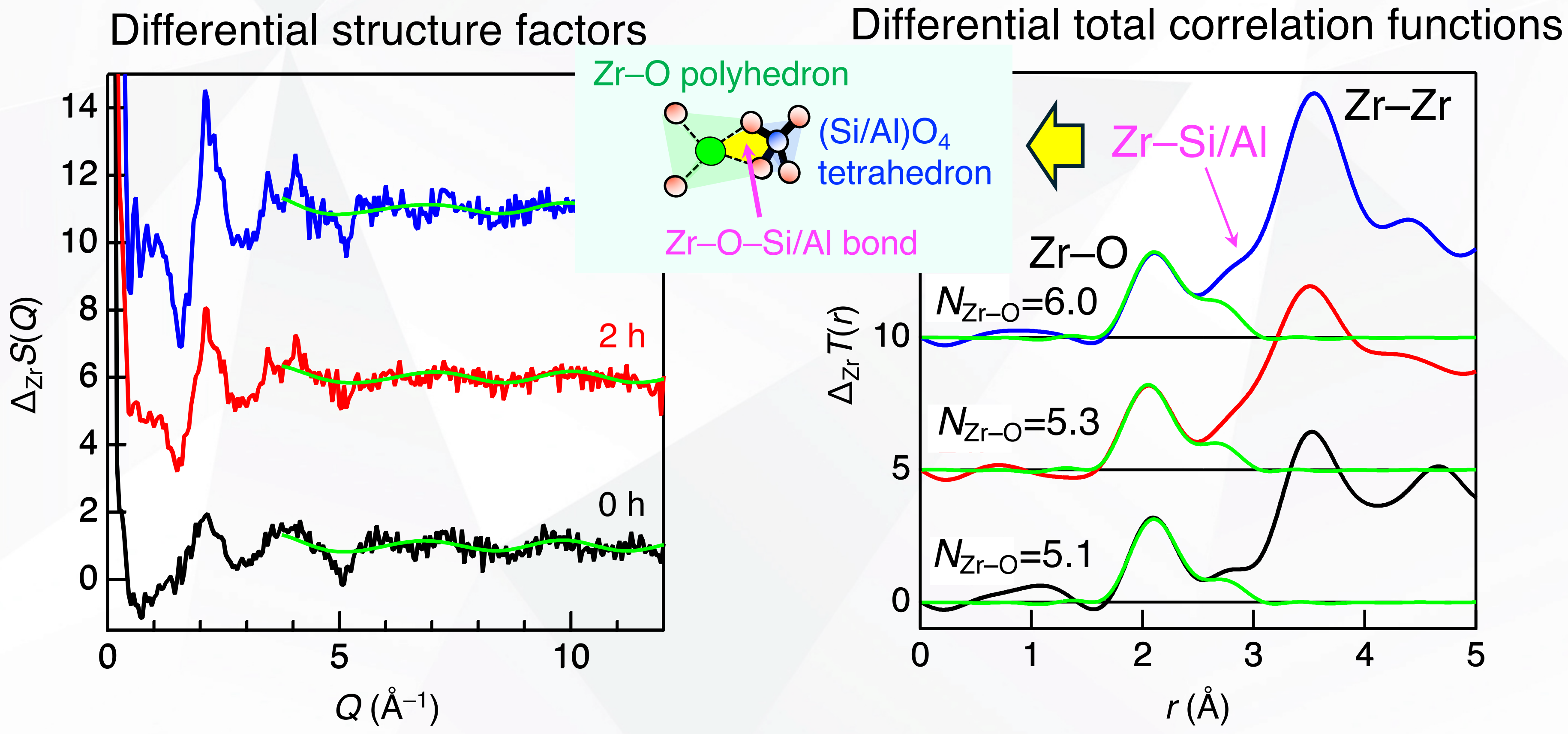


✓ The lower-Q behavior of $\Delta_{Zr}I_{coh}(Q)$ supported the SAXS data

✓ The Zr-related structure at short- and intermediate-range scales underwent changes upon thermal treatment

*S. Kohara *et al.*, J. Phys. Condens. Matter, **17**, S77 (2005).

AXS data (Zr K-edge)
– short- and intermediate-range structure analysis


Differential structure factors

Differential total correlation functions

✓Zr–O coordination number increased from 5.1 to 6.0 with increasing annealing duration

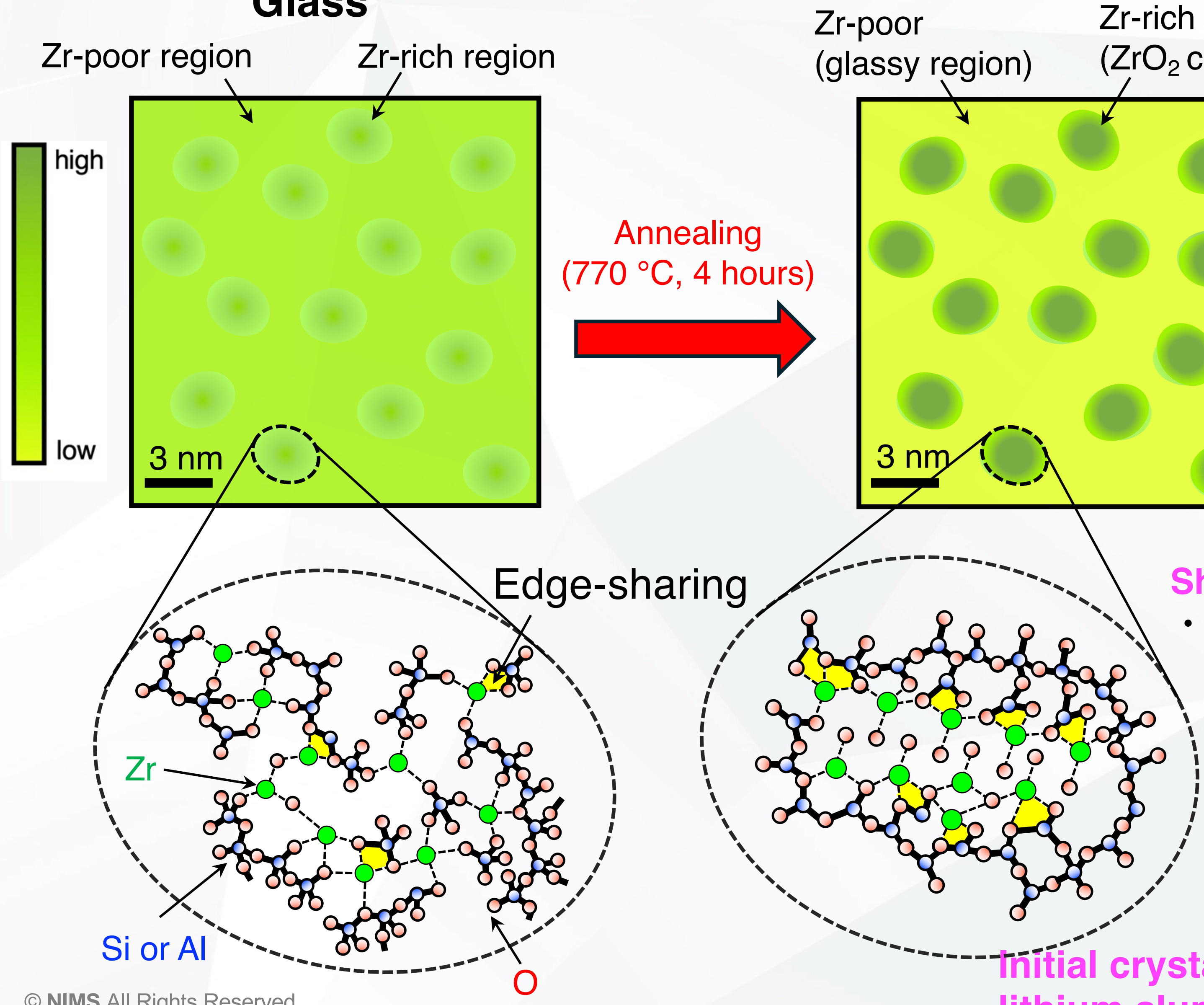
✓Edge-sharing between ZrO_x polyhedron and $(Si/Al)O_4$ tetrahedron
→ not a typical structural feature of glass-forming materials

$$\Delta_{\mathrm{Zr}}S(Q) \\ = 0.033S_{\mathrm{ZrZr}}(Q) + 0.312S_{\mathrm{ZrSi}}(Q) + 0.117S_{\mathrm{ZrAl}}(Q) + 0.018S_{\mathrm{ZrLi}}(Q) + 0.015S_{\mathrm{ZrNa}}(Q) + 0.521S_{\mathrm{ZrO}}(Q)$$

Nanoscale and intermediate-range structures of pristine glass and 4-h-annealed glass-ceramics

Glass

Glass-ceramic (4 h annealed)



Nanometer scale

- **Increase in contrast in Zr concentration between Zr-poor and Zr-rich regions**
- **Formation of ZrO_2 crystal nucleus in Zr-rich region**

Short–intermediate range scale

- **Formation of Zr–O–Si/Al bonds between ZrO_2 crystal nucleus and glassy region (edge-sharing ZrO_x and $(Si/Al)O_4$)**

Initial crystal nucleus for the Zr-doped lithium aluminosilicate glass-ceramic

Summary

1. We succeeded in characterizing the network topology in densified SiO_2 glasses in terms of persistent homology. The distinct features in the network topology indicate that open structure of glass is collapsed, leading to ordering of Si atoms manifested by the evolution of FSDP.
2. We constructed the most reliable structural models for the alkali silicate glasses by using the combined RMC–MD method and succeeded in reconsidering the mixed alkali effect based on the behaviors of the alkali ions around the NBO atoms as well as the modification of the Si–O network by the addition of alkali oxides.
3. Anomalous X-ray scattering data showed the formation of edge sharing between the ZrO_x polyhedra and $(Si/Al)O_4$ tetrahedra during the initial nucleation stage of aluminosilicate glass. The local structure of Zr resembled a cubic or tetragonal ZrO_2 crystalline phase and formed after 2 h of annealing the pristine glass (the initial crystal nucleus for the Zr-doped lithium aluminosilicate glass-ceramic).