

EXPRESS LETTER

Bond angle distributions in silica polymorphs

Shinji Kohara^{1,†}, Yohei Onodera¹, Motoki Shiga^{2,3,1,4}, Hirokazu Masai^{5,1},
Atsunobu Masuno^{6,1}, Koji Kimura^{7,1} and Koichi Hayashi⁷

¹Center for Basic Research on Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305–0047, Japan

²Unprecedented-scale Data Analytics Center, Tohoku University, Sendai 980–8578, Japan

³Graduate School of Information Sciences, Tohoku University, Sendai 980–8579, Japan

⁴RIKEN Center for Advanced Intelligence Project, Chuo-ku, Tokyo 103–0027, Japan

⁵Department of Materials and Chemistry, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka 563–8577, Japan

⁶Graduate School of Engineering, Kyoto University, Kyoto 615–8520, Japan

⁷Department of Physical Science and Engineering, Nagoya Institute of Technology, Gokisocho, Showaku, Nagoya 466–8555, Japan

Bond angle distributions (BADs) in silica crystals, silica glass, and siliceous zeolites were compared to understand the topology of silica polymorphs. It is found that the Si–O–Si bond angle is 180° in β -cristobalite, which is characteristic of highly symmetrical sixfold rings. In contrast, the Si–O–Si BAD of silica glass, obtained from a molecular dynamics–reverse Monte Carlo model, has an average value of 153° with a full width at half maximum (FWHM) of 20°. The Si–Si–Si BAD of β -cristobalite exhibits a peak at 110° demonstrates that SiSi₄ hyper tetrahedra possess high symmetry. This feature is consistent with the presence of symmetric six-membered rings in β -cristobalite. On the other hand, both coesite and silicalite-1 (MFI) shows a variety of bond angles like silica glass, which is consistent with the variation of (Si–O)_n ring size.

Keywords: Silica polymorphs, Glass, Siliceous zeolite, Structure, Bond angle distribution

[Received June 10, 2026; Accepted June 23, 2026; Published online July 14, 2026]

Silica is one of the most important oxide materials¹⁾ that exhibits various polymorphs and readily forms glass.²⁾ The fundamental structural motif of silica crystals is corner-sharing SiO₄ tetrahedra, although high-pressure phases exhibit octahedral or higher coordination numbers.³⁾ This corner-sharing tetrahedral motif is preserved in both silica glass and siliceous zeolites. Structural modifications under high pressures and high temperatures have been extensively studied using various experimental and simulation techniques.²⁾

We have been investigating the topology and homology of silica polymorphs, focusing on (Si–O)_n ring size distributions, cavity volumes, and ring shapes.^{4–6)} The bond angle distribution (BAD) is a crucial structural parameter for understanding the network structure of silica. In particular, the Si–O–Si bond angle distribution in silica glass remains a subject of ongoing debate.^{7,8)}

In this report, we compare the BADs of silica crystals, siliceous zeolites, and silica glass.

Calculations of BADs were performed for various crystal structures [α -cristobalite,⁹⁾ β -cristobalite,¹⁰⁾ α -quartz,¹¹⁾ coesite,¹²⁾ siliceous zeolite, faujasite (FAU),¹³⁾ sodalite (SOD),¹⁴⁾ and silicalite-1 (MFI)^{15)]} and the atomic

configuration of silica glass obtained from molecular dynamics (MD)–reverse Monte Carlo (RMC) simulations.¹⁶⁾

The continuous distribution is discretized into a histogram with a bin width of $\Delta\theta$. The probability density of finding an angle in the interval $[\theta - \Delta\theta/2, \theta + \Delta\theta/2]$ is calculated as:

$$P(\theta) = \frac{N(\theta)}{N_{\text{total}} \Delta\theta}, \quad (1)$$

where $N(\theta)$ is the number of triplets falling within the bin centered at θ , and N_{total} is the total number of identified triplets satisfying the cutoff condition $r \leq R_c$. The solid-angle-corrected probability density $g(\theta)$ for each bin is calculated as

$$g(\theta) = \frac{P(\theta)}{\sin \theta}. \quad (2)$$

The R_c values for Si–Si, Si–O, and O–O are 3.20, 1.85, and 2.80 Å for the crystal, and 3.50, 1.90, and 3.00 Å for the glass, respectively. The BADs were calculated within the range of $6.05^\circ < \theta < 173.95^\circ$.

Before discussing BADs, the ring size distributions in a series of silica polymorphs⁴⁾ calculated using King¹⁷⁾ and primitive^{18,19)} criteria, are shown in Fig. S1. Note that the King criterion is based on the shortest path, whereas the primitive criterion is suitable for detecting larger rings, as a

[†] Corresponding author: S. Kohara; E-mail: KOHARA.Shinji@nims.go.jp

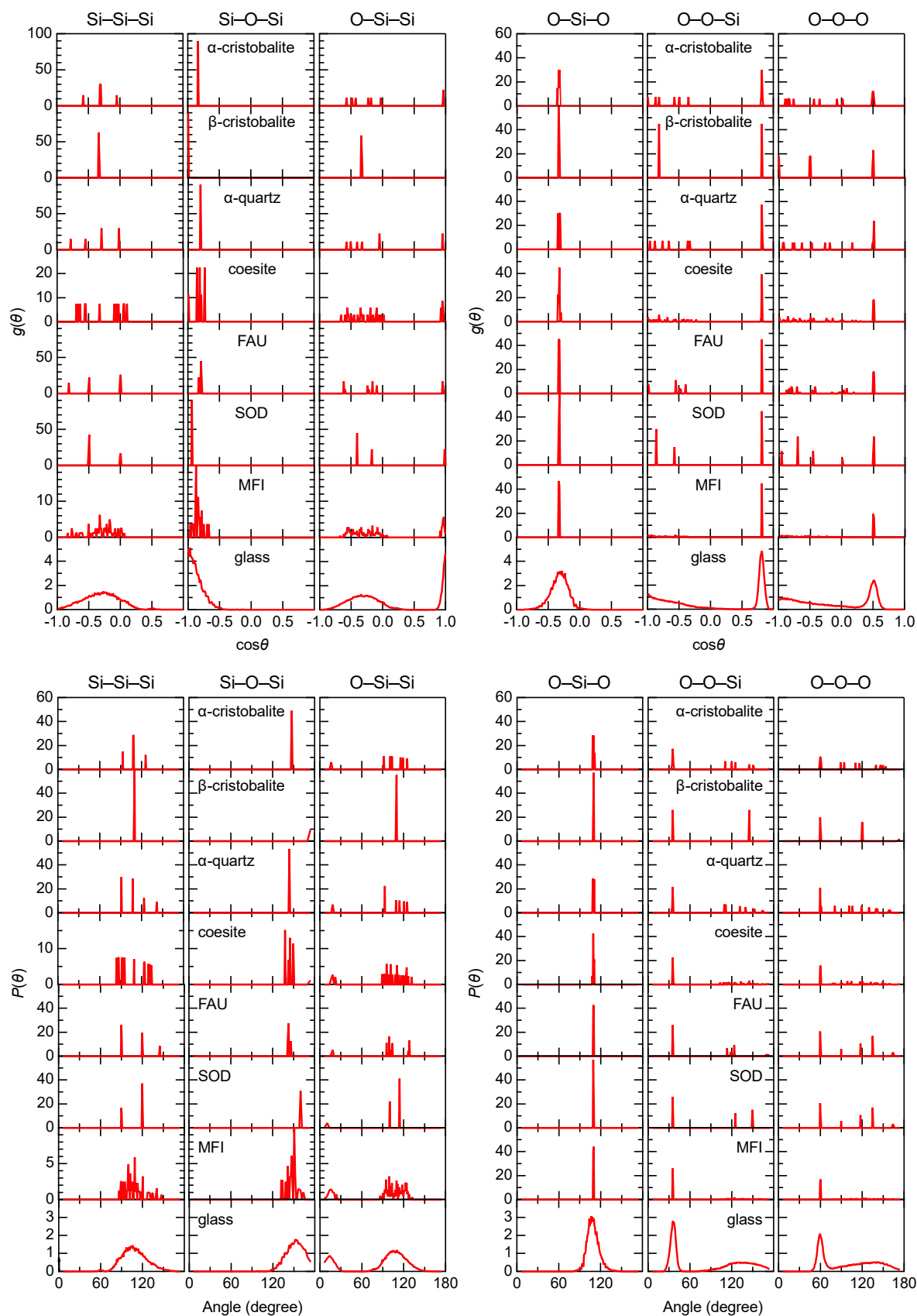


Fig. 1. Bond angle distributions, $P(\theta)$ (lower) and solid-angle-corrected bond angle distributions, $g(\theta)$ (upper), of silica polymorphs.

primitive ring is defined as one that cannot be decomposed into two smaller rings. As discussed in Ref. 3), cristobalites possess only sixfold rings consisting of six SiO_4 tetrahedra, whereas silica glass shows a broad ring size distribution ranging from three to tenfold rings, although sixfold rings dominate when using the primitive criterion. According to Gupta,²⁰⁾ this broad ring size distribution is topologically disordered. On the other hand, α -quartz possesses large fraction of eightfold rings in addition to sixfold rings and coesite possesses a variety of ring sizes similar to silica glass, which is consistent with the results reported in a previous study.¹⁹⁾ Siliceous zeolites also possess a variety of ring sizes similar to coesite, and the primitive criterion can detect effectively the large rings formed by silicalite cages.

Figure 1 shows the BADs, $P(\theta)$ (lower), and the solid-angle-corrected BADs, $g(\theta)$ (upper), of silica polymorphs. Note that the right and left panels show intratetrahedral and intertetrahedral correlations, respectively. All samples show a peak centered at $\theta = 109^\circ$ ($\cos \theta = -0.33$) in the O–Si–O BADs, owing to the formation of SiO_4 tetrahedra.

The O–O–O BAD of β -cristobalite exhibits two prominent peaks at $\theta = 60^\circ$ ($\cos \theta = 0.50$, intratetrahedral) and 120° ($\cos \theta = -0.50$, intertetrahedral). The O–O–Si BAD of β -cristobalite also exhibits two prominent peaks at $\theta = 35^\circ$ ($\cos \theta = 0.82$, intratetrahedral) and 145° ($\cos \theta = -0.82$, intertetrahedral). Peaks at higher angles are less prominent in other samples, suggesting that β -cristobalite has extremely high symmetry, which agrees well with our previous results derived from persistent homology analysis.⁴⁾

All samples except FAU and SOD show peaks centered at $\theta = 109.4^\circ$ ($\cos \theta = -0.33$) in the intertetrahedral Si–Si–Si BADs, owing to the formation of SiSi_4 hypertetrahedra.⁴⁾ In particular, β -cristobalite exhibits a very sharp profile, suggesting that the SiSi_4 hypertetrahedra are highly symmetric. This is consistent with the fact that its sixfold rings are highly symmetric and the order parameter q of the SiSi_4 hypertetrahedra is high in β -cristobalite.⁴⁾

The intertetrahedral O–Si–Si BAD of β -cristobalite exhibits a sharp peak at 110° ($\cos \theta = -0.34$). In contrast, other samples exhibit two broad peaks at around 109° ($\cos \theta = -0.33$) and 16° ($\cos \theta = 0.96$). This tetrahedral bond-angle distribution arises from the high symmetry of the SiSi_4 hypertetrahedra in β -cristobalite. The most striking feature in the intertetrahedral Si–O–Si BADs is that the bond angle of β -cristobalite is 180° (enlarged figures are shown in **Fig. 2**). Note that this specific angle cannot be evaluated by our calculation code for $g(\theta)$ because it leads

to division by zero ($\sin 180^\circ = 0$, see Eq. 2). This bond angle also indicates that sixfold rings in β -cristobalite are highly symmetric. Silica glass exhibits a very broad Si–O–Si bond angle distribution owing to its inherent disorder, whereas both coesite and MFI also exhibit broad distributions, likely due to the distribution of ring sizes as shown in Fig. S1. Consequently, we suggest that there is a correlation between topological disorder and broad intertetrahedral Si–O–Si bond angle distributions. Gaussian fitting of the $P(\theta)$ data for the glass yields an average value of 153° with a full width at half maximum (FWHM) of 20° . A comparison of these results with those of previous studies^{7,8,21–25)} using MD simulations, machine-learning potential MD (MLMD) simulations, X-ray diffraction (XRD), and neutron diffraction (ND) is presented in **Table 1**. Our results agree well with those obtained from RMC modeling based on ND data.

In this article, we present the BADs of a series of silica polymorphs. We found that the BAD of β -cristobalite

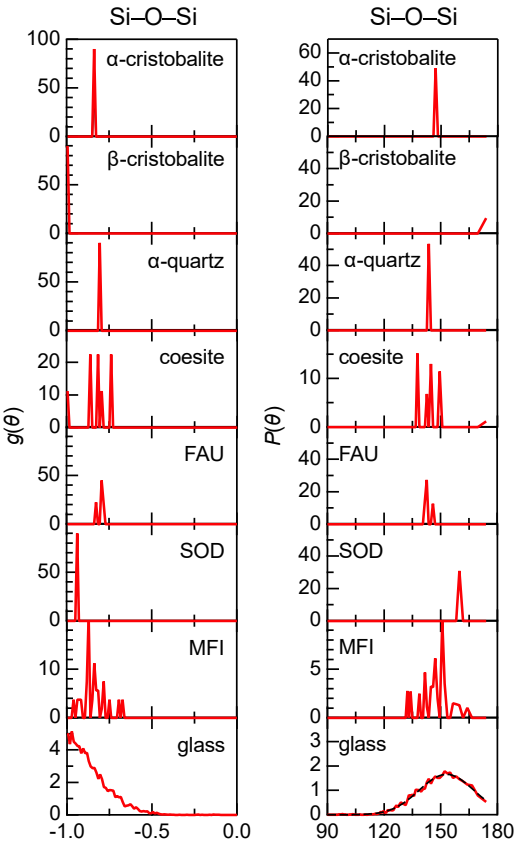


Fig. 2. Enlarged view of the Si–O–Si BADs for silica polymorphs. The curve fit for the glass data is shown as a black curve.

Table 1. Comparison of Si–O–Si BADs obtained using different methods

	MD–RMC (this work)	MD (BKS) ⁷⁾	MD (VSL) ⁷⁾	MD (VKRE) ²¹⁾	ML MD ²⁴⁾	RMC (ND) ⁸⁾	XRD ²²⁾	XRD ND ²³⁾	NMR ²⁵⁾
Mean value (degree)	153	152	147	142	145	151	144	147	142
FWHM (degree)	20	36	10	25	—	20	38	17	26

exhibits a highly symmetrical topology, whereas the topologies of both coesite and MFI are similar to that of silica glass. This feature suggests that the dynamics of MFI is very similar to that of coesite, which in turn resembles that of silica glass in terms of the boson peak observed in inelastic neutron scattering data.²⁶⁾

Acknowledgment This work was supported by JSPS Grants-in-Aid for Transformative Research Areas (A) “Hyper-Ordered Structures Science” (Grant Numbers 20H05878, 20H05880, 20H05881, 20H05882, and 20H05884).

References

- 1) P. J. Heaney, C. T. Prewitt and G. V. Gibbs, *Rev. Mineral.* **29**, 1 (1994).
- 2) G. N. Greaves and S. Sen, *Adv. Phys.* **56**, 1 (2007).
- 3) Y. Kuwayama, K. Hirose, N. Sata and Y. Ohishi, *Science* **309**, 923 (2005).
- 4) S. Kohara, S. Sato, M. Shiga, Y. Onodera, H. Masai, T. Wakiyama, A. Masuno, A. Hirata, N. Kitamura, Y. Idemoto, K. Kimura and K. Hayashi, *J. Ceram. Soc. Jpn.* **132**, 653 (2024).
- 5) S. Kohara, *J. Ceram. Soc. Jpn.* **133**, 488 (2025).
- 6) S. Kohara, K. Kimura, M. Shiga, Y. Onodera, A. Hirata and K. Hayashi, *J. Ceram. Soc. Jpn.* **134**, 208 (2026).
- 7) X. Yuan and A. N. Cormack, *J. Non-Cryst. Solids* **319**, 31 (2003).
- 8) M. G. Tucker, D. A. Keen, M. T. Dove and K. Trachenko, *J. Phys.-Condens. Mat.* **17**, S67 (2005).
- 9) J. J. Pluth, J. V. Smith and J. Faber, *J. Appl. Phys.* **57**, 1045 (1985).
- 10) R. W. G. Wyckoff, *Z. Krist.-Cryst. Mater.* **62**, 189 (1926).
- 11) K. Kihara, *Eur. J. Mineral.* **2**, 63 (1990).
- 12) L. Levien and T. Prewitt, *Am. Mineral.* **66**, 324 (1981).
- 13) C. Baerlocher and L. B. McCusker, Database of Zeolite Structures, <http://www.iza-structure.org/databases>.
- 14) D. M. Bibby and M. P. Dale, *Nature* **317**, 157 (1985).
- 15) E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, *Nature* **271**, 512 (1978).
- 16) P. S. Salmon, A. Zeidler, M. Shiga, Y. Onodera and S. Kohara, *Phys. Rev. B* **107**, 144203 (2023).
- 17) S. V. King, *Nature* **213**, 1112 (1967).
- 18) D. S. Franzblau, *Phys. Rev. B* **44**, 4925 (1991).
- 19) C. S. Mariani and L. W. Hobbs, *J. Non-Cryst. Solids* **124**, 242 (1990).
- 20) P. K. Gupta, *J. Am. Ceram. Soc.* **76**, 1088 (1993).
- 21) J. P. Rino, I. Ebbsjö, R. K. Kalia, A. Nakano and P. Vashishta, *Phys. Rev. B* **47**, 3053 (1993).
- 22) R. L. Mozzi and B. E. Warren, *J. Appl. Crystallogr.* **2**, 164 (1969).
- 23) J. C. Neuefeind and K.-D. Liss, *Berich. Bunsen Gesell.* **100**, 1341 (1996).
- 24) K. Kobayashi, M. Okumura, H. Nakamura, M. Itakura, M. Machida, S. Urata and K. Suzuya, *Sci. Rep.* **13**, 18721 (2023).
- 25) R. F. Pettifer, R. Dupree, I. Farnan and U. Sternberg, *J. Non-Cryst. Solids* **106**, 408 (1988).
- 26) Y. Onodera, S. Kohara, P. S. Salmon, A. Hirata, N. Nishiyama, S. Kitani, A. Zeidler, M. Shiga, A. Masuno, H. Inoue, S. Tahara, A. Polidori, H. E. Fischer, T. Mori, S. Kojima, H. Kawaji, A. I. Kolesnikov, M. B. Stone, M. G. Tucker, M. T. McDonnell, A. C. Hannon, Y. Hiraoka, I. Obayashi, T. Nakamura, J. Akola, Y. Fujii, K. Ohara, T. Taniguchi and O. Sakata, *NPG Asia Mater.* **12**, 85 (2020).