# Supporting Information

## Lithium coordination disorder controlling ionic conductivity in mixed-halide borate glasses

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## S1. Structural analysis of $B_2O_3$ glass

The neutron and X-ray $S(Q)$ for $B_2O_3$ glass are shown in Fig.S1(a). $B_2O_3$ glass exhibits a first sharp diffraction peak (FSDP) observed at $Q \sim 1.6$ Å$^{-1}$ in both the neutron and X-ray $S(Q)$, indicating the formation of an intermediate-range order comprising a B–O covalent network.[1–3] A sharp secondary principal peak (PP) is observed at $Q \sim 3$ Å$^{-1}$ in X-ray $S(Q)$, while the PP in neutron $S(Q)$ is not prominent (fig. S1(a)). This observation can be attributed to the consideration that the PP reflects the packing of oxygen atoms in oxide glassy materials,[4] i.e., the weighting factor of O–O correlations for X-rays is greater than that for neutrons. The total correlation functions, $T(r)$, for $B_2O_3$ glass, as derived from the Fourier transforms of the neutron and X-ray $S(Q)$ data, are shown in Fig. S1b. A high real-space resolution was achieved in the neutron $T(r)$ due to the Fourier transform of the $S(Q)$ with the high maximum $Q$ value ($Q_{max}$) of 40 Å$^{-1}$. The $T(r)$ data for both the X-ray and neutron clearly show the B–O correlation peak at 1.37 Å. The second peak observed at 2.38 Å in the X-ray and neutron $T(r)$ is attributed to the overlap of O–O and B–B correlations. The $S(Q)$ and $T(r)$ data, in conjunction with the results derived from the pair function method (illustrated as black broken curves), are shown in Figs. S1(a) and 1(b), respectively. In the pair function analysis, B–O, O–O, and B–B pairs were adopted to reproduce the first and second peaks in $T(r)$. As shown in Fig. S1a, a good agreement between the pair function and the experimental $S(Q)$ was achieved at $Q > 4.8$ Å$^{-1}$. The structural parameters for B–O, O–O, and B–B correlations obtained using the pair function method are summarized in Table S1. The B–O coordination number was found to be 3.0, which is identical to the results in previous studies,[1,2] indicating a triangular $BO_3$ motif is the local structural unit in $B_2O_3$ glass. The O–O and B–B coordination numbers were found to be 4.0 and 3.0, respectively. These results are consistent with the reported structure of $B_2O_3$ glass, in which trigonal planar $BO_3$ triangles form a network by sharing their vertex oxygen atoms. [1–3]

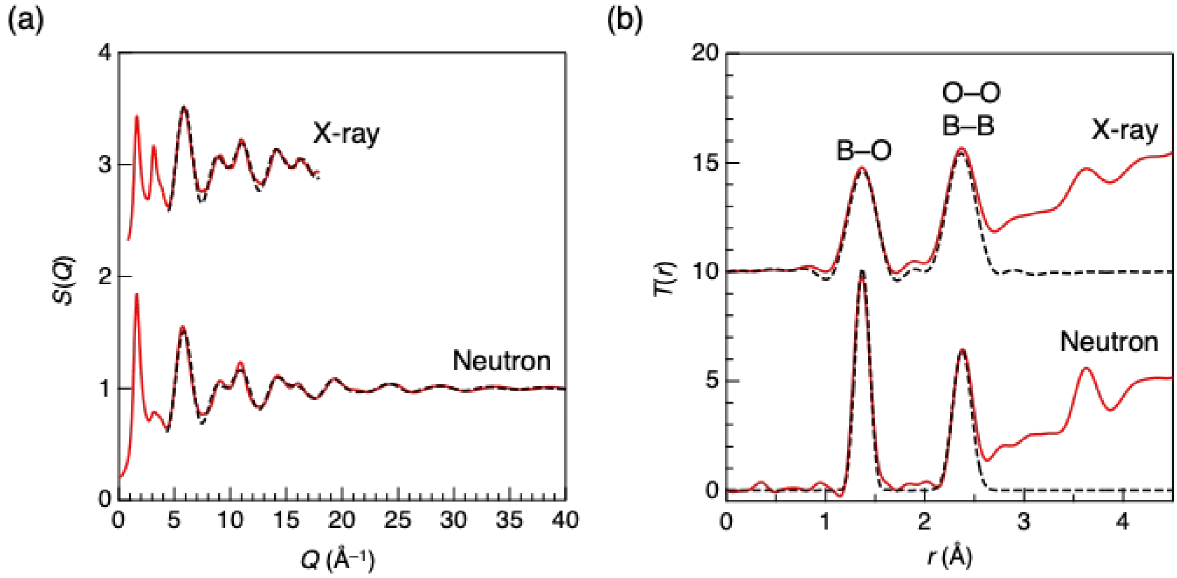


**Fig. S1 X-ray and neutron diffraction data of $B_2O_3$ glass in (a) *Q*-space and (b) real-space.** Red solid curves represent experimental data, and black broken curves represent calculated data by the pair function method.

**Table S1 Structural parameters for $B_2O_3$ glass derived from neutron (X-ray) diffraction data**

| | B–O | O–O | B–B |
|---|---|---|---|
| $r_{\alpha-\beta}$ (Å) | 1.37 (1.37) | 2.38 (2.37) | 2.38 (2.37) |
| $N_{\alpha-\beta}$ | 3.0 (3.0) | 4.0 (4.0) | 3.0 (3.0) |

## S2. $^{11}$B MAS NMR spectroscopy

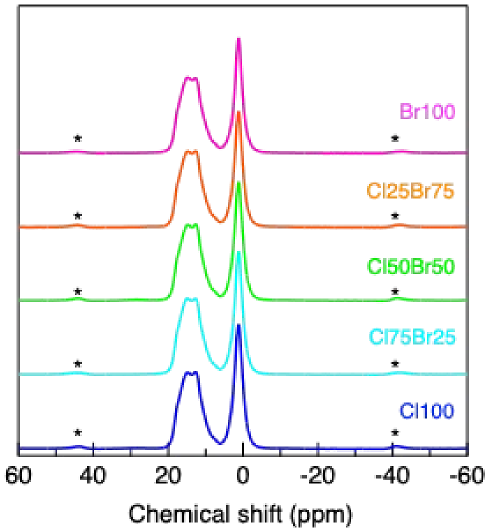


**Fig. S2 $^{11}$B MAS NMR spectra for the $1/3Li_2O–1/3B_2O_3–1/3LiCl_xBr_{1–x}$ glasses.** Spinning side bands are marked by asterisks.

**Table S2 The fraction of $BO_3$ and $BO_4$ units in the $1/3Li_2O–1/3B_2O_3–1/3LiCl_xBr_{1–x}$ glasses derived from $^{11}$B MAS NMR spectra**

| | $BO_x$ fraction (%) | |
|---|---|---|
| | $BO_3$ | $BO_4$ |
| Br100 | 59 | 41 |
| Cl25Br75 | 60 | 40 |
| Cl50Br50 | 60 | 40 |
| Cl75Br25 | 61 | 39 |
| Cl100 | 63 | 37 |

## S3. Coordination number analysis of X-ray diffraction data

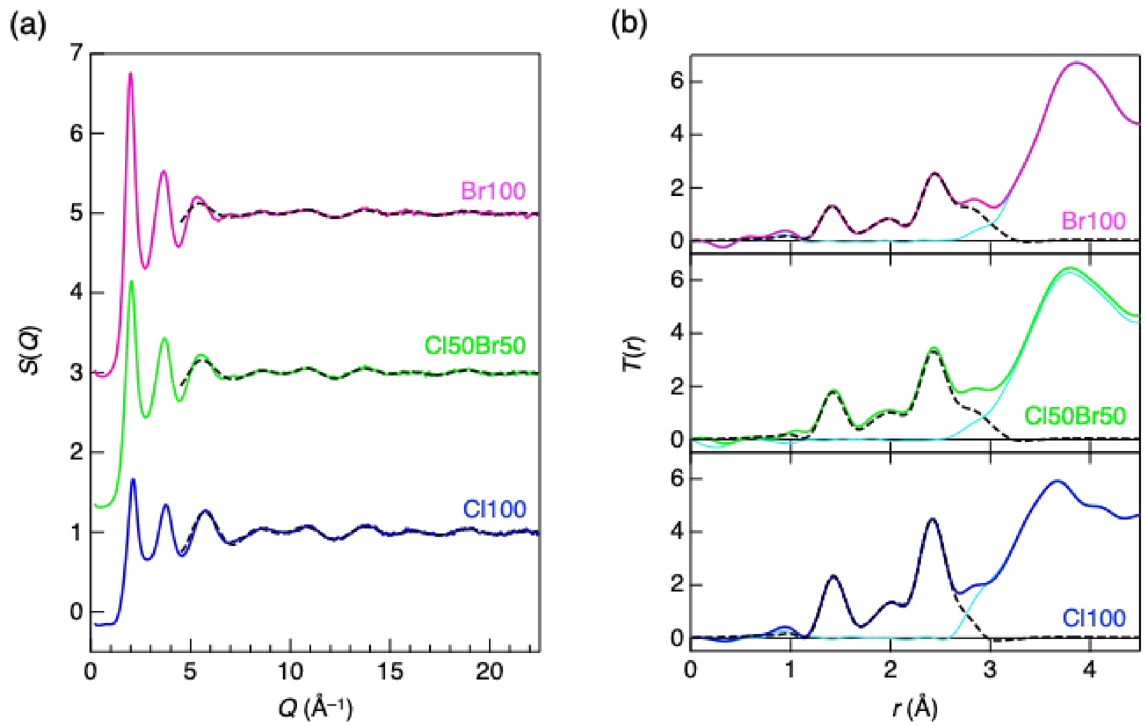


**Fig. S3 X-ray diffraction data of the 1/3Li$_2$O–1/3B$_2$O$_3$–1/3LiCl$_x$Br$_{1–x}$ glasses in (a) *Q*-space and (b) real-space.** Colored solid curves and black broken curves represent experimental and calculated data, respectively. The differences between experimental and calculated data are plotted as cyan curves.

**Table S3 Structural parameters for Li-related correlations in the 1/3Li$_2$O–1/3B$_2$O$_3$–1/3LiCl$_x$Br$_{1–x}$ glasses, derived from X-ray diffraction data**

| | Li–O (1) | | Li–O (2) | | Li–Cl | | Li–Br | | Li–B | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $r_{Li–O}$ (Å) | $N_{Li–O}$ | $r_{Li–O}$ (Å) | $N_{Li–O}$ | $r_{Li–Cl}$ (Å) | $N_{Li–Cl}$ | $r_{Li–Br}$ (Å) | $N_{Li–Br}$ | $r_{Li–B}$ (Å) | $N_{Li–B}$ |
| Br100 | 1.96 | 2.2 | 2.37 | 0.9 | – | – | 2.65 | 2.0 | 2.99 | 3.1 |
| Cl50Br50 | 1.96 | 2.3 | 2.30 | 0.9 | 2.45 | 1.3 | 2.65 | 1.0 | 2.94 | 3.2 |
| Cl100 | 1.98 | 2.4 | 2.30 | 0.8 | 2.44 | 1.8 | – | – | 2.82 | 3.1 |

**Table S4 Structural parameters for B–O, O–O, B–B correlations in the 1/3Li$_2$O–1/3B$_2$O$_3$–1/3LiCl$_x$Br$_{1–x}$ glasses, derived from X-ray diffraction data**

| | B–O (1) | | B–O (2) | | O–O | | B–B | |
|---|---|---|---|---|---|---|---|---|
| | $r_{B–O}$ (Å) | $N_{B–O}$ | $r_{B–O}$ (Å) | $N_{B–O}$ | $r_{O–O}$ (Å) | $N_{O–O}$ | $r_{B–B}$ (Å) | $N_{B–B}$ |
| Br100 | 1.41 | 3.0 | 1.64 | 0.4 | 2.42 | 3.6 | 2.42 | 2.4 |
| Cl50Br50 | 1.42 | 3.0 | 1.62 | 0.4 | 2.42 | 3.6 | 2.41 | 2.4 |
| Cl100 | 1.42 | 2.8 | 1.63 | 0.6 | 2.42 | 3.6 | 2.42 | 2.4 |

## References


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