Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Preparation and characterization of sodium-ion conductive Na_3BS_3 glass and glass-ceramic electrolytes

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Table S1 Atomic coordinates of the Na_3BS_3 crystal[18].

Phase			Na_3BS_3			
Crystal System			Monoclinic			
Spase Group			$C\ 2/c$ (No. 15)			
Lattice Parameter, Volume, Z			a = 11.853 Å, b = 6.664 Å, c = 8.406 Å, V = 585.274 Å^3			
			α = 90, β = 118.18, γ = 90, Z = 4			
Atoms	x	y	z	Site	Occupancy	
Na1	0.40274(6)	0.21349(9)	0.49570(8)	8f	1.0000	
Na2	0.25000	0.25000	0.00000	4c	1.0000	
S1	0.50000	0.14347(6)	0.25000	4e	1.0000	
S2	0.13550(3)	0.05790(5)	0.25321(4)	8f	1.0000	
B	0.50000	0.4217(3)	0.25000	4e	1.0000	

Table S2 Ionic conductivities at 25 °C (σ_{25}) and activation energy (E_a) for conduction of sodium-ion conducting glassy electrolytes.

Composition	σ_{25} / S cm^{-1}	E_a / kJ mol^{-1}	Ref.
Na_3PO_4	3.2×10^{-10}	133	20
Na_3BO_3	1.5×10^{-8}	61	13
Na_3PS_4	6.0×10^{-6}	47	5
$Na_4P_2S_7$	1.6×10^{-6}	–	21
$NaPS_3$	3.0×10^{-7}	–	21
$Na_4B_2S_5$	4.4×10^{-7}	48	14

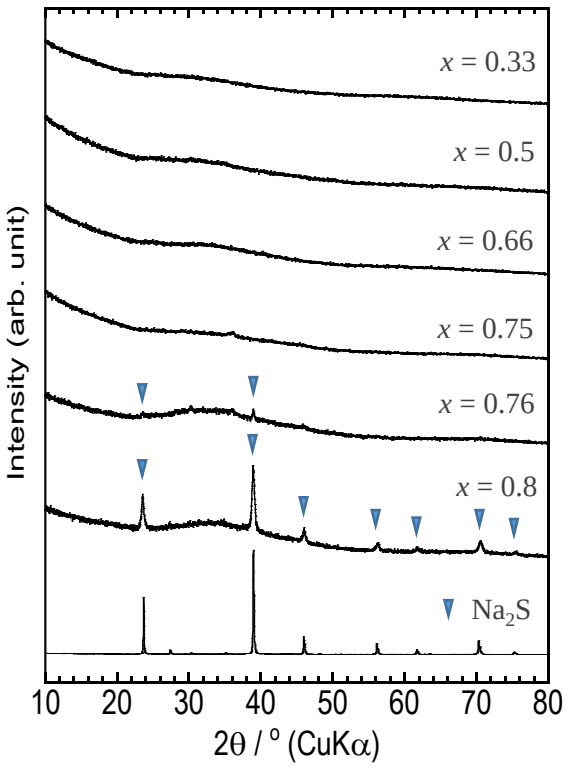


Fig. S1 XRD patterns of xNa$_2$S·(1-x)B$_2$S$_3$ glass electrolytes synthesized via a mechanochemical process from the crystal corresponding to each composition.

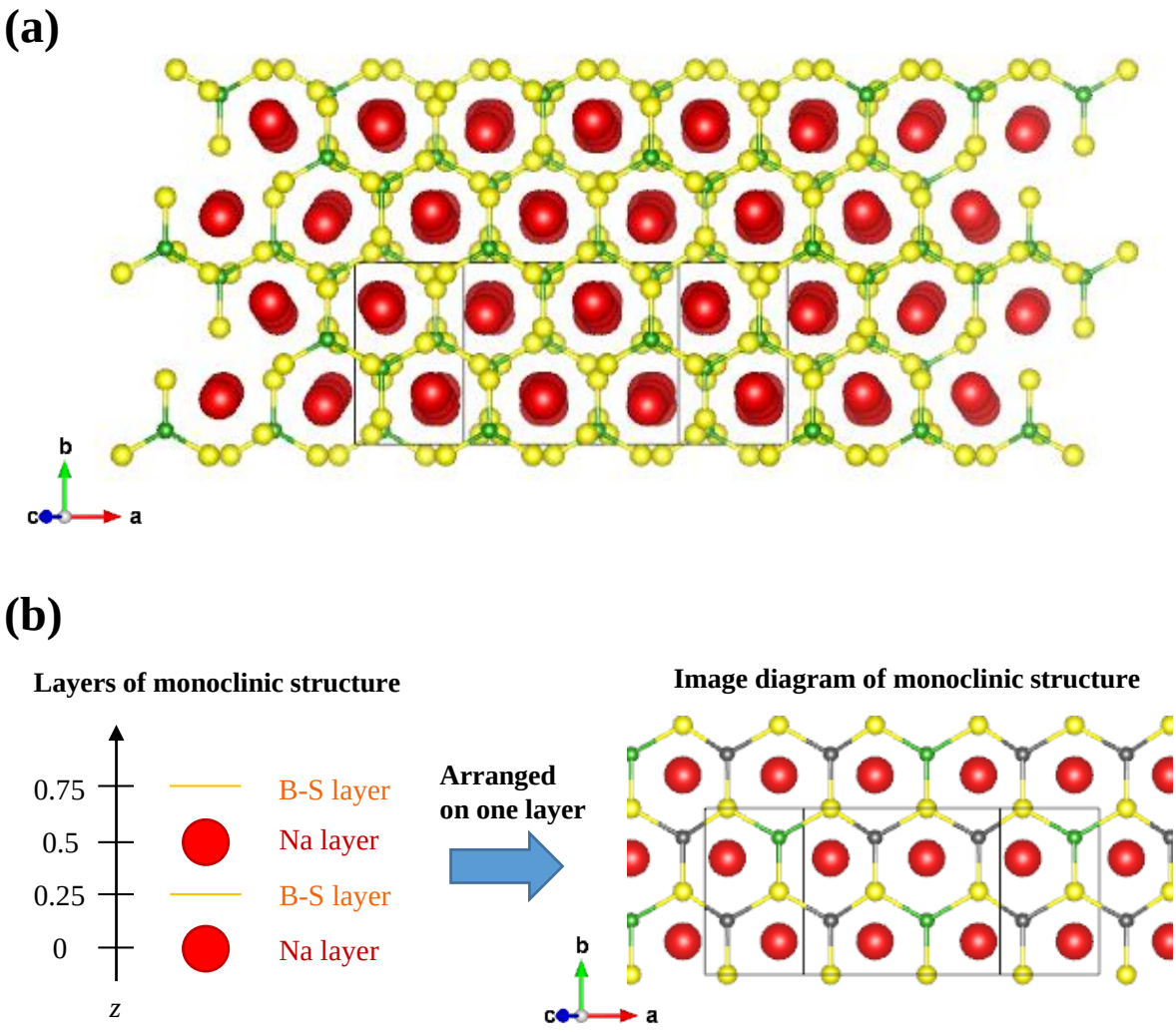


Fig. S2 (a) Schematic diagram of the crystal structure of monoclinic Na_3BS_3.[18] The red, green, and yellow spheres are Na, B, and S, respectively. (b) Image diagram of the monoclinic structure. The Na layers and B–S layers located at different z-positions are shown on the left. The right shows the arrangement of atoms in one layer. The B sites of the B–S layers are 1/3 occupied. Three-coordinated unoccupied B sites are shown as gray spheres.

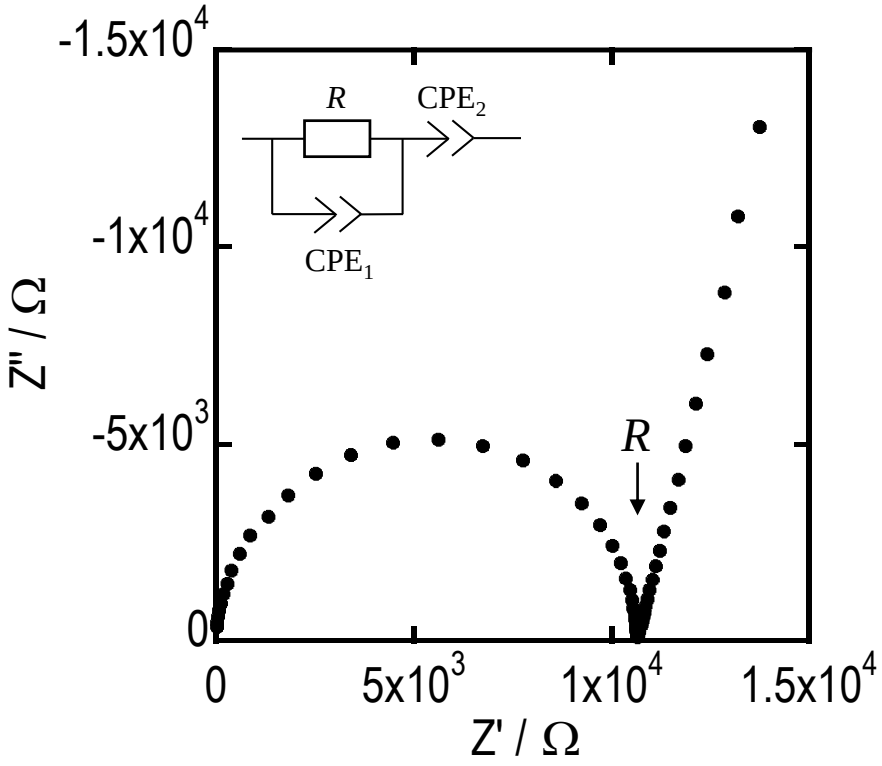


Fig. S3 Nyquist plot at 30 ˚C of Na_3BS_3 glass.

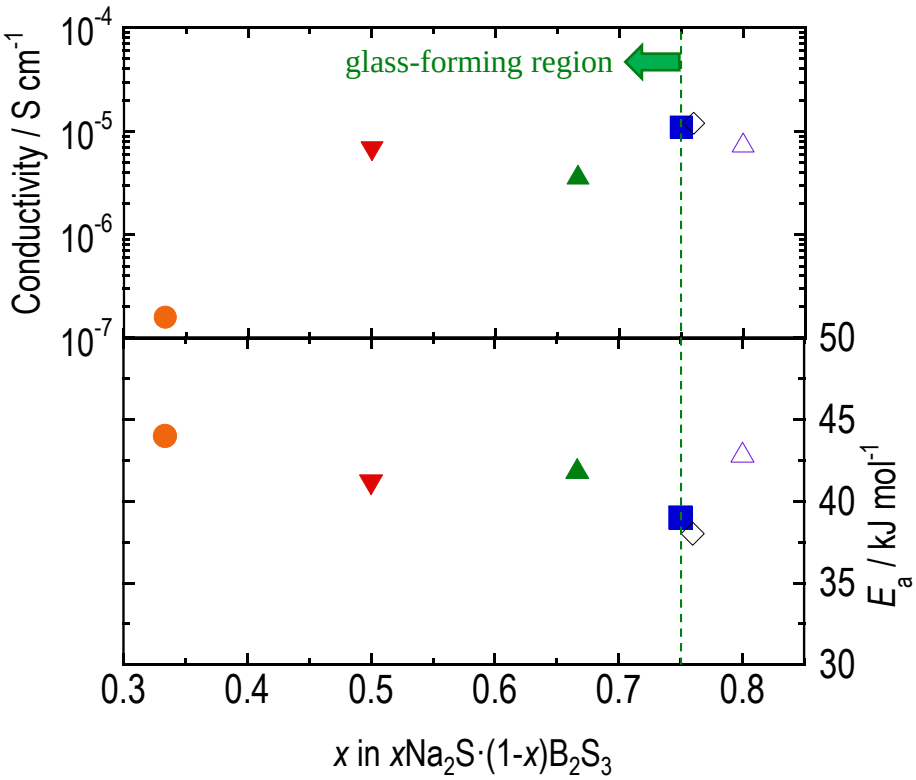
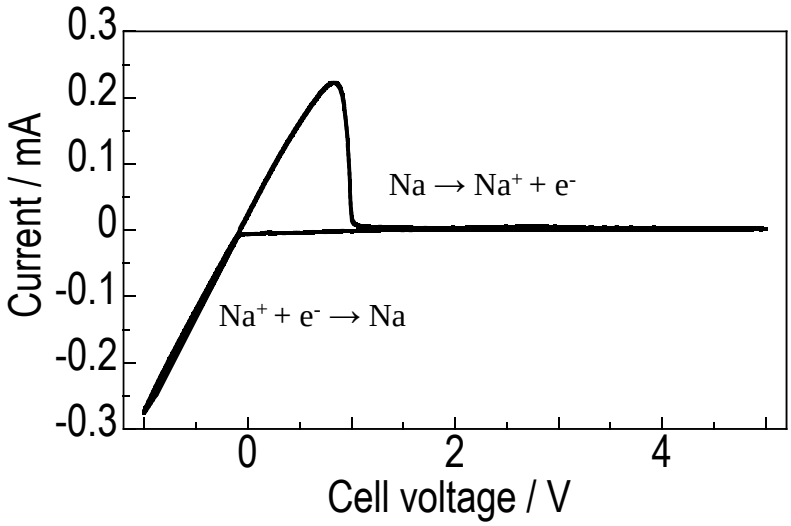


Fig. S4 Room-temperature ionic conductivities and activation energies (E_a) for conduction of xNa$_2$S·(1-x)B$_2$S$_3$ glass electrolytes.

(a)



(b)

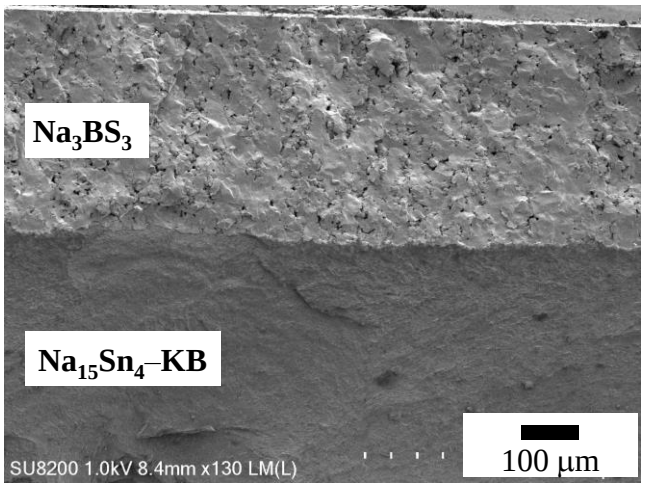


Fig. S5 (a) Cyclic voltammogram of the Na_3BS_3 glass. Stainless–steel and $Na_{15}Sn_4$–KB was used as working and counter electrodes, respectively. The potential sweep was performed with a scanning rate of 5.0 mV min^{-1} at 60 ˚C. (b) Cross-sectional SEM image of the cell after cyclic voltammetry. The working electrode of stainless steel was removed from the cell and two layers of Na_3BS_3 / $Na_{15}Sn_4$–KB are observed.