A sodium-ion sulfide solid electrolyte with unprecedented conductivity at room temperature

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Solid electrolytes are key materials to enable solid-state rechargeable batteries, a promising technology that could address the safety and energy density issues. Here, we report a sulfide sodium-ion conductor, Na2.88Sb0.88W0.12S4, with conductivity superior to that of the benchmark electrolyte, Li10GeP2S12. Partial substitution of antimony in Na3SbS4 with tungsten introduces sodium vacancies and tetragonal to cubic phase transition, giving rise to the highest room-temperature conductivity of 32 mS cm\(^{-1}\) for a sintered body, Na2.88Sb0.88W0.12S4. Moreover, this sulfide possesses additional advantages including stability against humid atmosphere and densification at much lower sintering temperatures than those (>1000 °C) of typical oxide sodium-ion conductors. The discovery of the fast sodium-ion conductors boosts the ongoing research for solid-state rechargeable battery technology with high safety, cost-effectiveness, large energy and power densities.
Development of all-solid-state rechargeable batteries has been desired because they have superior characteristics, such as a long cycle life, high safety, high-energy density, and high rate capability. To realize bulk-type solid-state batteries using electrodes and electrolyte particles, superior solid electrolytes with high ionic conductivity and good ductility are desired, as they can facilitate wide contact areas with active materials simply upon pressing, without a high-temperature-sintering process. Sulfide solid electrolytes meet this demand. Among solid electrolytes, Li-ion conductivity of over $10^{-2}$ cm$^{-2}$ s$^{-1}$ is much lower than the Li-ion conductivity of LGPS, which is $2.5 \times 10^{-2}$ cm$^{-2}$ s$^{-1}$ in 2012. Li-ion conductivity of $>10^{-4}$ cm$^{-2}$ s$^{-1}$ has not been observed in the spectra of Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ (Supplementary Fig. 1). Cross-section of the pelletized Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ heated at 275 °C for 12 h was observed by field-emission scanning electron microscopy (FE-SEM), and the secondary electron (SE) and backscattered electron (BSE) images are shown in Fig. 1c.

As no composition-dependent contrast is observed in the BSE image, all the elements including tungsten are assumed to be uniformly dispersed in the monitored cross-section. In addition, energy-dispersive X-ray spectroscopic (EDX) mapping indicates the presence of tungsten in the entire SEM area (Supplementary Fig. 2). Elemental analysis using Rutherford backscattering spectrometry (RBS) predicts that the composition is Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$, which is almost the same as the nominal composition of Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$.

Here we report a sulfide Na-ion conductor with ionic conductivity higher than the best Li-ion conductivity of 2.5 × 10$^{-2}$ cm$^{-2}$ s$^{-1}$. As for electrolytes with typical NASICON structure, the Na-ion conductivity in Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ is higher than the Li-ion conductivity in NASICON-type Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (no. 12), which implies that the Na-ion mobility in solid electrolytes is inherently higher than the Li-ion mobility. This is because of the weaker Lewis acidity of Na ions, which have weaker electrostatic interaction with the oxide or sulfide anion species constituting the crystalline structure. However, Na-ion conducting sulfide electrolytes with the same degree of conductivity as that of the best Li ion conductor, LGPS, have not been discovered.

Here we report a sulfide Na-ion conductor with ionic conductivity higher than the best Li-ion conductivity of 2.5 × 10$^{-2}$ cm$^{-2}$ s$^{-1}$ in LGPS-type Li$_{0.75}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.34}$ (no. 12). As for electrolytes with typical NASICON structure, the Na-ion conductivity in Na$_{2.9375}$PS$_{3.9375}$Cl$_{0.0625}$ is higher than the Li-ion conductivity in NASICON-type Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (no. 12), which implies that the Na-ion mobility in solid electrolytes is inherently higher than the Li-ion mobility. This is because of the weaker Lewis acidity of Na ions, which have weaker electrostatic interaction with the oxide or sulfide anion species constituting the crystalline structure. However, Na-ion conducting sulfide electrolytes with the same degree of conductivity as that of the best Li ion conductor, LGPS, have not been discovered.

### Results

**Material synthesis and structure analysis.** A mechanochemical process using a planetary ball mill apparatus was used to directly produce crystalline Na$_{2}$Sb$_{3}$S$_{4}$ (Supplementary Fig. 6a), and its crystallinity increased after heat treatment at 275 °C for durations ranging from 1.5 to 12 h. X-ray diffraction (XRD) patterns of the Na$_{3-3x}$Sb$_{1-x}$W$_x$S$_4$ (x = 0 and 0.12) electrolytes prepared by heat treatment are shown in Fig. 1a. The three Raman bands around 360, 380, and 410 cm$^{-1}$ in the Raman spectrum (Fig. 1b) of the prepared Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ reveals the presence of Sb$_3$$^{3-}$ units, while the Raman band at ~470 cm$^{-1}$ corresponds to the presence of WS$_4$$^{2-}$ units, which are typically observed for crystalline Na$_2$WS$_4$. A fairly weak peak at ~420 cm$^{-1}$, probably due to WS$_4$, is observed in the spectrum of Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ heated for 1.5 h, while no peak is observed for that heated for 12 h. The Raman bands of the other starting materials (Sb$_2$S$_3$, Na$_3$S, S$_8$) are not observed in the spectra of Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ (Supplementary Fig. 1). Cross-section of the pelletized Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ heated at 275 °C for 12 h was observed by field-emission scanning electron microscopy (FE-SEM), and the secondary electron (SE) and backscattered electron (BSE) images are shown in Fig. 1c.

**Conduction characteristics.** Conductivity of the pelletized Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ was measured by the AC impedance method. Pellets of the material were prepared by cold-pressing the electrolyte powder at 1080 MPa, followed by heat treatment at 275 °C. Figure 3a shows its conductivity at 25 °C ($\sigma_{25}$) and activation energy $E_a$ for conduction as functions of the duration of heating at 275 °C. As an example, Nyquist plots at −25 °C for the pellets heated for 1.5 and 12 h are shown in Supplementary Fig. 4a, and the cross-sectional SEM image of the pellets are shown in Supplementary Fig. 4b. Only a spike owing to the capacitance at the interface between each electrolyte pellet and Au current collector is observed; other resistance components are not clearly detected in the high-frequency region even at a low measurement temperature of ~−25 °C. In this study, the total conductivity is thus determined from the resistance at the intersection of the spike.
and the x-axis; this resistance refers to the total resistance including both the grain-bulk and grain-boundary components of the electrolytes.

The pellet heated for 1.5 h (relative density of 93%) has \( \sigma \) of \( 1.7 \times 10^{-2} \) S cm\(^{-1} \) and \( E_a \) of 19 kJ mol\(^{-1} \). The electronic conductivity at 25 °C measured by a DC polarization technique is \( 7.9 \times 10^{-8} \) S cm\(^{-1} \) or lower, as shown in Supplementary Fig. 5, which is five orders of magnitude lower than the total conductivity mentioned above; the Na-ion transport number of the prepared Na\(_{2.88}\)Sb\(_{0.88}\)W\(_{0.12}\)S\(_4\) is almost unity. Na-ion conductivity increased with an increase in the heating time as shown in Fig. 3a, because of the increase in the crystallinity of the cubic phase as well as the relative density of the pellet, as determined by the XRD analysis (Supplementary Fig. 6) and cross-sectional SEM imaging (Supplementary Fig. 4b). The best conducting behavior is obtained for a pellet with a...
relative density of 95% obtained after heating for 12 h, which shows the highest $\sigma_{25}$ of $3.2 \times 10^{-2}$ S cm$^{-1}$ and the lowest $E_a$ of 17 kJ mol$^{-1}$.

Further, the conductivity of the material is definitely affected by the tungsten content ($x$) of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$. Pellets of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ with varying $x$ were prepared by cold-pressing the milled Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ powders at 360 MPa, followed by heating at 275 °C for 1.5 h. XRD patterns of these pellets indicate the formation of cubic crystals without any impurity phases at all the compositions (Supplementary Fig. 7b). No apparent peak shift in the XRD patterns is observed with increasing $x$. This is probably because of the nearly same ionic radii of Sb$^{5+}$ and W$^{6+}$. The temperature-dependence of conductivities of the prepared pellets obeys the Arrhenius equation (Supplementary Fig. 6c). The conductivity increases and the activation energy decreases with an increase in $x$, and better conductive behavior is achieved for $x$ ranging from 0.12 to 0.15 (Supplementary Table 3). The electrolyte with $x = 0.12$ gives the lowest $E_a$ of 21 kJ mol$^{-1}$ and a high conductivity of 6.4 × 10$^{-3}$ S cm$^{-1}$, which is superior to those of Na$_3$SbS$_4$ ($x = 0$) ($\sigma_{25} = 2.1 \times 10^{-3}$ S cm$^{-1}$ and $E_a = 26$ kJ mol$^{-1}$). Although this comparison is carried out among the lower density pellets prepared at a smaller molding pressure and a shorter heating time, the partial substitution of tungsten for antimony definitely improves the Na-ion conductivity of the Na$_3$SbS$_4$ electrolyte.

The Arrhenius plot of the Na-ion conductivity of the Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ electrolyte developed in this study is shown in Fig. 3b; it shows the highest conductivity among Na-ion conductors reported so far. In addition, $\sigma_{25}$ of $3.2 \times 10^{-2}$ S cm$^{-1}$ for the electrolyte is higher than that of the best LGPS-type Li$_2$S$_4$Si$_{1.5}$P$_{1.44}$S$_{11.5}$Cl$_{0.3}$ Li-ion conductor ($\sigma_{25} = 2.5 \times 10^{-2}$ S cm$^{-1}$). Here, we have successfully discovered for the first time, a Na-ion conducting sulfide electrolyte that has higher conductivity than all known Li-ion conductors.

Exposure to the atmosphere. Another advantage of the Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ electrolyte is its high tolerance to air; that is, the amount of harmful H$_2$S generated when it is exposed to air is almost negligible. H$_2$S generation from the electrolyte even under a highly humid environment (relative humidity, R.H. of 70%) is suppressed when compared to that from a conventional Na$_3$PS$_4$ under a less-humid condition with R.H. of 50% (Fig. 4). An XRD pattern similar to that of the hydrate, Na$_3$SbS$_4$·9H$_2$O is observed for the electrolyte after exposure to humid air (Supplementary Fig. 8). The formation of a hydrate compound without H$_2$S generation has already been reported for crystalline Na$_3$SbS$_4$; our tungsten-substituted sulfide conductor also undergoes a similar structural transformation with hydration.

Discussion

In conclusion, a Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ superionic conductor was developed. The conductivity of this material, $3.2 \times 10^{-2}$ S cm$^{-1}$ is the highest among sulfide Li and Na-ion conductors reported so far. The generation of Na vacancies and stabilization of the cubic phase by the partial substitution of antimony in Na$_3$SbS$_4$ with tungsten are responsible for its superior conduction. The Na$_{2.88}$Sb$_{0.88}$W$_{0.12}$S$_4$ electrolyte with high tolerance to H$_2$S gas generation under an ambient atmosphere would improve safety of all-solid-state batteries and reduce manufacturing cost. The developed sulfide superionic conductor contributes to the realization of solid-state batteries with high-energy density and power density.
Method

**Material synthesis.** Na_{2-x}Sb_{x/2}W_{3/4}S_{4} solid electrolytes were prepared via a mechanochemical process using a planetary ball mill apparatus (Pulverisette 7, Fritsch GmbH). Reagent-grade Na_{2}S (Nagao Co., 99.1%), Sb_{2}S_{3} (Nihonseiko Co., 99.8%), WS_{3} (Aldrich Chem. Co., 99%), and S (Aldrich Chem. Co., 99.98%) powders were used as the starting materials. The starting materials were weighed at stoichiometric compositions of Na_{2-x}Sb_{x/2}W_{3/4}S_{4} (e.g., the molar ratio of Na_{2}Sb_{x/2}W_{3/4}S_{4} = 0.00167:0.33:3.3 for Na_{2}Sb_{2}W_{3}S_{12}, the molar ratio of Na_{2}Sb_{2/3}W_{3/4}S_{3}:W_{5}S_{12} = 48.0:14.7:33.3:3.4 for Na_{2}Sb_{2/3}W_{3}S_{12}S_{12}). A mixture of the starting materials (0.6 g) was ground using a mortar and a pestle for 10 min and placed in a 45 mL ZrO_{2} pot containing 250 ZrO_{2} balls of diameter 4 mm. Then, the starting materials were milled at a rotation speed of 510 rpm for 5 or 30 h. It was further subjected to heat treatment at 275 °C for several hours (1.5–18 h) in a porcelain crucible to obtain the final Na_{2-x}Sb_{x/2}W_{3/4}S_{4} electrolytes. The colors of the prepared electrolytes Na_{2}Sb_{3}S_{4} and Na_{2}Sb_{2/3}W_{3}S_{12}S_{12} were brown and dark brown, respectively. All the steps were carried out in dry Ar atmosphere.

**Material characterization.** The crystallographic phase was identified using an X-ray diffractometer (SmartLab, Rigaku) with Cu-Kα radiation. Diffraction data were collected in steps of 0.02° in the 2θ range 10–60° at a scan rate of 10° min^{−1}. X-ray diffraction (XRD) measurements were performed using an airjet with a beryllium window to prevent the sample from exposure to air. The crystalline structure was refined using the computer program PDXL2 (Rigaku Co.), and the crystal models were visualized using the VESTA software. Rietveld refinement was performed for the XRD data collected in steps of 0.02° in the 2θ range 10–120° at a scan rate of 2° min^{−1}. For this, the first, the peak shape, background coefficient, scale factor, and lattice constants were refined. Then, the occupancy refined at the stoichiometric composition, and the atomic displacement factor was refined. Finally, the above parameters were fixed, and the occupancy, except for sulfur, was refined.

Raman spectroscopy was carried out on a Raman spectrophotometer (LabRAM HR-800, Horiba) equipped with a 532 nm He-Ne laser to identify the structural units. The electrolyte samples were placed in an airjet with dry Ar gas, and Raman scattering signals from the samples were collected through a transparent quartz plate mounted on the upper side of the vessel. Scanning electron microscopy was carried out on a FE-SEM (SU8220, Hitachi High-Tech.) equipped with an energy-dispersive X-ray spectroscopy system (EDX, EMAXEvolution X-MAX, Horiba Ltd.). The samples were transferred from an airjet with dry Ar gas to the apparatus.

The chemical composition was determined by RBS. The RBS measurement was carried out with He^{+} beam accelerated to 2.3 MeV using customized RC-43 (National Electrostatics Co.). The sample was set in a high-vacuum chamber (Pulverisette 7, Fritsch GmbH). The sample was cold pressed at 360 or 1080 MPa into pellets and then heated at 250–380 °C for 1.5 h. The amount of H_{2}S was normalized by the mass of sulfur in the samples. According to the RBS measurement, the prepared electrolytes Na_{3}SbS_{4} and Na_{2.88}Sb_{0.88}W_{0.12}S_{4} were brown and dark brown, respectively.

The electronic conductivity was measured on electrolyte pellet samples via a DC polarization technique. The data were collected using a potentiostat/galvanostat (1287, Solartron) with the applied DC voltages ranging from 0.07 to 0.98 V at 25 °C.

**Data availability**

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
A.H. conceived and designed the work and wrote the paper. N.M. performed the material synthesis and characterization. S.Y., F.T., and C.H. conducted XRD analysis, Rietveld refinement, and SEM analysis. A.S., A.H., and M.T. supervised the research. All authors participated in discussions and know the implications of the work.

Competing interests
The authors declare no competing interests.

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