Vacancy-Contained Tetragonal Na₃SbS₄ Superionic Conductor

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The growing demand for high capacity rechargeable batteries used in large-scale energy storage,[1] including electric vehicles and electrical grid energy storage, has promoted the development of sodium all-solid-state batteries.[2] As a type of solid electrolyte (SE), sulfide superionic conductors have been attracted worldwide attention because of its relatively high room temperature ionic conductivity as well as low grain-boundary resistance achieved by directly cold-pressing the sulfide powders, which makes them favorable to assemble all-solid-state batteries.[3] Significant progress has been made in lithium sulfide electrolytes in recent years.[2,3,4] However, in spite of the similar characteristic to lithium, the milestone of sulfide sodium superionic conductors as a room-temperature SE was ambiguous until Hayashi and co-workers introduced cubic Na₃PS₄ with ionic conductivity of 0.2 mS cm⁻¹ in 2012,[5] and subsequently 0.46[6] and 0.74[7] mS cm⁻¹ by using high purity starting materials and Si doping, respectively. These values are two orders of magnitude higher than that of tetragonal Na₃PS₄.[8] After that, impressive breakthroughs on both theoretical and experimental researches have been achieved for sulfide-based sodium SEs.[9] Nonetheless, there are much fewer sodium superionic conductors in contrast to lithium sulfides; their room-temperature ionic conductivities remain low. Exploration of sodium sulfides with ionic conductivity over 1 mS cm⁻¹ is highly anticipated.

Ceder and co-worker proposed design principles for superionic conductors and suggested that the anion sulphur sublattices analogous to body-centered cubic (bcc) frameworks allow the migration of ions with a lower activation barrier than in other close-packed frameworks, thus resulting in fast ion diffusion.[10] Moreover, cell volume has been reported to play an important role in either Na⁺ or Li⁺ transport, such as the latest works on Se.[9e] and Sn-doped[9e] Na₃PS₄ (with expanded unit cell) as well as cation-substituted Li₀.₉₆GeP₂S₁₂ (LGPS).[11] Very recently, theoretical investigations on both Na₃PS₄[9e] and Na₃PSe[9f] revealed that a defect-driven diffusion mechanism (either Na⁺ interstitial or Na⁺ vacancy) accounts for the high ionic conductivity, while the stoichiometric compounds showed negligible diffusivity. Actually, Na⁺ deficiency is the reality during synthesis as it is a very reactive metal. Therefore, an ultrafast ion diffusion is expected if the conductor meets the prerequisites of large cell volume, low migration barrier energy, and/or sodium vacancy defects.

In this study, Na₃SbS₄ with a tetragonal structure was synthesized and evaluated for the first time. An expanded unit cell containing distorted-cubic sulphur sublattices was identified. Moreover, the existence of Na vacancies in Na₃SbS₄ structure was revealed, experimentally verifying the vacancy theory recently proposed.[9f] This tetragonal Na₃SbS₄ demonstrates a high ionic conductivity of 3 mS cm⁻¹ and is the fastest room temperature Na⁺ solid conductor to date.

The Rietveld refinement results for X-ray diffraction (XRD) pattern of synthesized Na₃SbS₄ is shown in Figure 1a. The halo patterns at low angle reflect the polyimide film. The crystal structure was determined to be tetragonal with the space group P4₂/c (No. 114) with two formula units per unit cell. To the best of our knowledge, this tetragonal Na₃SbS₄ has not been reported yet. The plots (Figure 1a) of the observed, calculated, and difference patterns from the Rietveld refinement prove undoubtedly the formation of single-phase tetragonal Na₃SbS₄. Table 1 lists the refined structural data and refinement parameters. The cell parameters of Na₃SbS₄ are a = 7.1597(5) Å and c = 7.2906(6) Å, larger than those of tetragonal Na₃PS₄ (a,b = 6.9520 (4) Å, c = 7.0757(5) Å)[8] and Si-doped cubic Na₃PSe₄ (a = 6.9978 Å).[12] While lower than that of cubic Na₃PSe₄ (a = 7.3094(2) Å).[9f] Tetragonal Na₃SbS₄ is just slightly deviated from its cubic symmetry[11] by elongating c axis.

Surprisingly, unlike other sodium sulfides showing stoichiometric composition, Rietveld refinement revealed the vacancy existence at Na₂ sites (see Table 1), experimentally verifying the defect hypothesis previously proposed.[9e-g] The occupancy of Na₂ sites contains 80% Na plus 20% vacancies rather than full occupancy of Na. The mole fraction of vacancies in Na₃SbS₄ is calculated to be 2.5%, comparable to the hypothesis value of 2.1% for Na₃PSe₄ assumed by Bo et al.[9f] With theoretical calculation,[9f] Ceder and co-workers found that vacancy defect has the lowest formation energy among different
defects evaluated and is the key factor for accelerating Na\(^{+}\) diffusion in Na\(_3\)PSe\(_4\). A extrapolated ionic conductivity as high as \(28.9 \text{ mS cm}^{-1}\) at room temperature for Na\(_3\)PSe\(_4\) with 2.1 mol.% Na vacancies was reported.\(^{[9g]}\)

The crystal structures of tetragonal Na\(_3\)SbS\(_4\) along various viewing directions are given in Figure 1b. The crystallographic unit cell consists of two SbS\(_4\) tetrahedral groups, with Sb atoms sit on 2\(_b\) sites and S atoms on 8\(_e\) sites. The Sb–S distance is 2.3619 Å and the S–Sb–S angles are 109.77° and 108.88°, indicating a slightly distorted regular tetrahedron and deviation of Sb atoms from the center of the tetrahedron. In contrast to cubic Na\(_3\)SbS\(_4\) where Na atoms situate simply at 6\(_b\) site,\(^{[13]}\) tetragonal Na\(_3\)SbS\(_4\) shows two independent Na positions: Na\(_1\) at 4\(_d\) and Na\(_2\) at 2\(_a\) sites (Table 1). Linear (Na\(_1\)) or zigzag (Na\(_1\) and Na\(_2\)) rows of Na\(^{+}\) occupy the interstices composed of the SbS\(_4\) tetrahedrons. The former locates in the channels parallel to the crystallographic \(c\) axis (left panel to Figure 1b) while the latter in the channels parallel to \(a\) or \(b\) axis (middle panel to Figure 1b). All these Na\(^{+}\) diffusion channels construct along 3D pathways orthogonal to each other. It is notable that the sulphur sublattices (inset of middle panel to Figure 1b) demonstrate an intensely distorted cubic lattice. This anion framework may benefit Na\(^{+}\) diffusion followed the mechanism similar to the bcc-sublattice-contained superionic conductors described in previous study.\(^{[10]}\) Different coordinations are observed for these two types of Na\(^{+}\), i.e., Na at Na\(_1\) and Na\(_2\) sites bound to six and eight sulphur atoms, respectively, as shown in the right panel to Figure 1b. The Na\(_1\)–S distances are 2.80, 3.07, and 3.13 Å and the Na\(_2\)–S distances are 3.02 and 3.38 Å.

Considering the existence of vacancies, the expanded unit cell, and the cubic-like sulphur sublattices, it is not surprising that the isotropic atomic displacement parameter (\(U_{\text{iso}} = B_{\text{iso}}/8\pi^2\)) of Na at either Na\(_1\) (0.022(4) Å\(^2\)) or Na\(_2\) (0.024(6) Å\(^2\)) sites is significantly larger than those for Sb (0.005(1) Å\(^2\)) and S (0.011(3) Å\(^2\)), as listed in Table 1. Fast Na\(^{+}\) diffusion is consequently highly expected.

Figure 1c shows the Raman spectrum of Na\(_3\)SbS\(_4\) at room temperature. The prominent resonance peaks observed over the measured range are attributed to the Sb–S vibrations of the isolated SbS\(_4\) group and obviously different from those of SbS\(_4\) group,\(^{[14]}\) confirming the successful formation of SbS\(_4\) group. The peaks at 402 (\(\nu_s\)), 382 (\(\nu_v\)), and 359 (\(\nu_s\)) cm\(^{-1}\) are
assigned to the stretching vibration modes and those at 189 (δ3) and 135 (δ2) are assigned to the deformational vibration modes of Sb–S(4).[14a] Neither phase transition nor decomposition is observed from differential scanning calorimetry (DSC) profile until 342 °C with a small endothermic peak (Figure 1d), confirming the thermal stability of tetragonal Na3SbS4. The endothermic reaction may be related to a decomposition of impurity phase that is out of the resolution of XRD.

Scanning electron microscopy (SEM) images for the morphology of Na3SbS4 pellets from hand-ground and ball-milled powders are displayed in Figure 2. The cold-pressed pellet from hand-ground powders shows more or less isolated grains with irregular shapes (Figure 2a), whereas that from ball-milled powders shows grains with more smooth shape and better connection (Figure 2b). However, the contacts between grains of the latter are inferior to those of ball-milled Na3PS4 reported previously.[15] Further optimization on preparation process to improve the pellet’s density is ongoing.

Arrhenius plot of the total ionic conductivity σ in the temperature range from 25 to 90 °C is depicted in Figure 3a for Na3SbS4. Nyquist plots of the impedance at different temperature are shown in the inset. The total ionic conductivity is calculated from the local minimal resistance at the intersection of the impedance spectrum. The relation logσ−1/T obeys the Arrhenius law, confirming a high purity and stable phase of the Na3SbS4 compound. The ionic conductivity locates in the range from 3 mS cm−1 at 25 °C to 16 mS cm−1 at 90 °C, approaching to those of organic liquid electrolytes currently used.[16] This value is three orders of magnitude larger than that of tetragonal Na3PS4[8] and significantly higher than those of state-of-the-art sulfides with cubic structure.[8c,d] The activation energy Eα for the sodium-ion conduction were determined from the slope of the linear Arrhenius plot using the equation:[15]

\[ \sigma = \sigma_0 \exp(-E_α/k_B T) \]

where σ0 represents the pre-exponential parameter and k_B the Boltzmann constant. The calculated activation energy of Na3SbS4 is 0.25 eV, comparable to those of LGPS and Na3PS4 sulfides.[3,16] Na3SbS4 with the high ionic conductivity and low activation energy can be considered as a promising SE used in all-solid-state sodium ion batteries.

The impedance spectrum of a solid ion conductor generally contains three distinct features, i.e., two semicircles at high and intermediate frequency and a Warburg-type region at low frequency, which are assigned to intragrain transport (bulk), intergrain transport (grain boundary), and capacitive behavior, respectively. In case of Na3SbS4, the semicircles (inset of Figure 3a) are hardly to be observed, especially measured at high temperature range, indicating a negligible intergrain transport. The inherently low grain boundary resistance is a typical characteristic of sulfides, which have the advantage to be assembled without heat treatment.[3,17] The steep linear spike at low frequency indicates that Na3SbS4 is a typical ionic conductor.[18]

Figure 2. SEM fracture images of Na3SbS4 cold-pressed from a) the melted ingot pulverized by hand grinding in an agate mortar and b) ball-milled powders.

**Table 1.** X-ray powder diffraction data (room temperature) for Na3SbS4 from Rietveld refinement; Biso values in (10^2 nm^2).

| Compound       | Na3SbS4 |
|----------------|---------|
| **Refined composition (at.%)** | Na3SbS4<sub>4</sub> |
| a = b, c (Å)   | 7.1597(5), 7.2906(6) |
| **Z**          | 2       |
| **Number of variables** | 51      |
| R<sub>1</sub>  | 0.064   |
| R<sub>2</sub>  | 0.084   |
| R<sub>wp</sub> | 0.078   |
| R<sub>0</sub>  | 0.049   |
| R<sub>δ2</sub> | 0.015   |
| Sb, in 2b (0, 0, 0), Biso | 0.40(9) |
| Na(1), in 4d (0, ½, z), Biso | 0.4412(16), 1.7(3) |
| Na(2), in 2a (0, 0, 0), Occ., Biso | 1.6(1)Na+0.4Cl<sup>-</sup>, 1.9(5) |
| S, in 8e (x, y, z), x, y, z, Biso | 0.2917(9), 0.3307(8), 0.1884(4), 0.9(2) |

<sup>a</sup>Z: number of formula units per unit cell.
the irreversible Na₃SbS₄/Pt side can be calculated by linear fitting the current–voltage curve in the voltage range from 3 to 5.5 V using the equation:

\[ \sigma_{\text{electronic}} = \frac{I_e}{S} \left( \frac{d|I_{\text{el}}|}{dE} \right) \]

where \(|I_{\text{el}}|\) is the total electronic current, \(E\) is the polarization voltage, \(S\) is the electrolyte–electrode surface area, and \(L\) is the electrolyte thickness. The calculated value is \(\sigma_{\text{electronic}} = 2 \times 10^{-8} \text{ mS cm}^{-1}\), eight orders of magnitude lower than the total ac conductivity (3 mS cm⁻¹). It thus can be concluded that \(\text{Na}^+\) practically reaches unity and ion can be regarded as the sole conductive species.

The electrochemical stability of Na₃SbS₄ with metallic sodium was evaluated using cyclic voltammetry (CV) measurement on a Pt/Na₃SbS₄/Na cell, as shown in Figure 3c. The potentials were scanned from −1 to 5 V versus Na/Na⁺ at a scan rate of 5 mV s⁻¹. The SE shows a broad electrochemical window up to 5 V, other than the sodium deposition and dissolution because of the cathodic and anodic reactions near 0 V versus Na/Na⁺, indicating a high decomposition potential. However, the low anodic peak suggests the deposited sodium is only partially stripped during the anodic reaction while the sodium remains reacted with the electrolyte to produce an inactive corrosion product. XRD patterns of Na₃SbS₄ before and after three cycles CV measurements are displayed in the inset of Figure 3c. No extra peak is observed after CV tests, suggesting a relative stability of Na₃SbS₄ against Na metal, e.g., Na₃SbS₄ is more stable against Na metal than Na₃PSe₄, whereas less stable than Na₃PS₄. Similar to the formation of Li₂S in lithium-sulfides against Li metal reported previously, small amount of Na₂S may form during the reduction process and act as a passivation layer mitigating the decomposition of Na₃SbS₄. The instability of Na₃SbS₄ toward metallic Na is a drawback of sulfide SEs. This issue could be solved through doping, surface decoration, and forming passivation layers. Our future work will concentrate on improving the stability of
Na₃SbS₄ against Na metal and assembling all-solid-state batteries using the Na₃SbS₄ solid electrolyte to investigate the electrochemical performance.

The hygroscopic characteristic of Na₃SbS₄ was investigated in air with 65% humidity. Figure 3d shows the XRD patterns for Na₃SbS₄ samples before (pristine) and after air-exposure for 5 h (air-5h) and followed by heating at 100 °C (air-5h 100 °C). Na₃SbS₄ absorbs the moisture in air and forms Na₃SbS₄·9H₂O (PDF#43-0442). Na₃SbS₄ is moisture sensitive similar to many other sulphides. Enhancement of air stability is feasible by appropriate materials’ design, as described in previously studies.[15,25] However, single phase tetragonal Na₃SbS₄ is fully recovered from dehydration of Na₃SbS₄·9H₂O at 100 °C, indicating a completely reversible hydration and dehydration process for Na₃SbS₄ which is favorable for Na₃SbS₄ preparation from solution as well as storage in air.

In summary, a new sodium superionic conductor tetragonal Na₃SbS₄ with the space group P32c was synthesized and investigated for the first time. Na atoms at both 2a and 4d sites demonstrate large isotropic atomic displacement parameters. Sulphur sublattices were found to be an intensely distorted cubic lattice. Most notably, the existence of 2.5 mol. % Na vacancies at Na2 sites (2a) was discovered and experimentally verifies previous hypothesis. Benefit from these favorable features, tetragonal Na₃SbS₄ shows prominent performance with fast ion diffusion. With a Na⁺ transference number approaching unity, the ionic conductivity reaches 3 mS cm⁻¹ at room temperature, the best value among state-of-the-art sodium sulphides to date to the best of our knowledge. Na₃SbS₄ is a promising candidate for practical application as an SE in all-solid-state sodium ion batteries.

Experimental Section

Synthesis of Na₃SbS₄: Na metal (AR, Sinopharm), Sb (99.999%, Sinopharm), and S (99.999%, Alfa) powder were mixed according to stoichiometric proportion of Na₃SbS₄ for sequential solid-state reaction. The mixture was loaded into a glassy carbon crucible, which was vacuum-sealed in a quartz tube, slowly heated to 700 °C in order to avoid exothermic reaction, dwelled for 12 h and cooled down naturally in the furnace. Based on our experiences, powders with coarse particles are not favorable for cold pressing. The resultant ingot was milled powders at 400 MPa. Indium foil was placed on both sides of ingot and assembled all-solid-state battery. Electrochemical Impedance Spectroscopy measurements were performed in the frequency range of 0.1 Hz to 2 MHz at room temperature using a Princeton P4000 impedance analyzer. The pellets for measurements were cold-pressed from milled powders at 400 MPa. Indium foil was placed on both sides of the pellets as electrodes. Stainless-steel rods were then attached to both sides as current collectors in an air-tight two-electrode cell. Wagner’s polarization measurements were performed at room temperature to determine the electronic contribution to the total conductivity on a Pt/Na₃SbS₄/Na cell. The cell was polarized by applying a constant dc potential (Princeton P4000) from 2 to 7 V across the Pt blocking electrode and the Na reversible electrode. The voltage was held at each step for 1000 s, approaching to a stationary state in each step of chronocoulometric experiment. The CV measurements were carried out at voltages ranging from −1 to 5 V with a scan rate of 5 mV s⁻¹ in an asymmetric Pt/Na₃SbS₄/Na cell, where Pt is a working electrode and Na a counter/reference electrode. A Faraday cage was used for all electrochemical measurements.

[Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-430596.]

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