Supplementary Figure 1 | Crystal with \((00l)\) cleavage along plane and X-ray diffraction

(a) The photograph of crystal specimen cleaved along \((00l)\) crystallographic planes. (b) The X-ray diffractogram recorded in Bragg-Brentano geometry for a \((001)\) crystal face, exhibiting the diffraction peaks corresponding only to the \((00l)\) planes. (c) The excellent \(K\alpha_1-\alpha_2\) splitting of the higher order diffraction peaks is observed, testifying to the high crystalline quality. A break in applied on the x-axis for an angular range.
Supplementary Figure 2 | The Raman spectra for $E_g$ and $A_{2g}$ phonons.

(a) Raman spectra measured on the (001) surface of Sn-BSTS and Bi$_2$Se$_3$ showing comparable mode widths. This is further confirmed by Lorentzian fits to the spectra, which include a defect induced mode and a two-phonon excitation. (b) Raman spectra are taken at 3 different locations named as SPOT A, SPOT B and SPOT C, 2mm apart, showing the excellent uniformity of the crystal, through reproducibility of the phonon spectra.
Supplementary Figure 3 | The ARPES spectra near Dirac cone

(a) Shows an extraction of the upper Dirac cone dispersions by using the $k$-positions (shown white dots) of the maxima in intensity of the ARPES spectrum for the potassium-deposited electron-doped sample. The red lines show the fitting of dispersions. (b) An elucidation of lower Dirac bands, by extrapolation of linear bands.
Supplementary Figure 4 | The ρ_{xx} and ρ_{yx} vs. (μ₀H sinθ)^{-1} plots

(a) and (b) are the magnetoresistance (MR) and Hall plots with inverse of magnetic field for one of the samples characterized. The schematic in the inset of figures shows the angle, θ, between magnetic field (represented by an arrow) and current in sample plane.
Supplementary Figure 5 | The synchrotron powder X-ray diffraction and lattice parameters

(a) The temperature dependent evolution of the synchrotron powder X-ray diffraction pattern for a powdered specimen of Sn-BSTS ($\lambda = 0.413727 \text{ Å}$) plotted for the data sequence recorded in the
temperature range of 2 – 90 K: data sequence-1 (vertical axis) is recorded at the temperature 2 K and data sequence-50 is recorded at 90 K. (b) The lattice parameters (a and c) determined by least squares fits to the observed diffraction patterns. (c) Cell volume plots for T = 20-90 K. No anomalous behavior is observed at ~50 K for any of the bulk crystal parameters. (error bars are smaller than the plotted points) The results indicate that no bulk structural transition occurs in Sn-BSTS in this temperature range.

**Supplementary Table 1**

<table>
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<th>Atom</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<td>0.21509(2)</td>
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<tr>
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<td>3a</td>
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</table>

\[ \begin{align*}
   a &= 4.21053(5) \text{ Å} \\
   c &= 29.55453(25) \text{ Å}
\end{align*} \]

\[ R_p = 10.2 \quad R_{wp} = 13.1 \quad R_{exp} = 6.63 \quad \chi^2 = 3.89 \]

The refined lattice parameters and atomic coordinates

**Supplementary Note 1 | Bulk crystal growth and structure analysis**

The high quality single crystal boule (~15 cm long) of Bi\textsubscript{1.08}Sn\textsubscript{0.02}Sb\textsubscript{0.9}Te\textsubscript{2}S (Sn-BSTS) (Figure 2a of main manuscript) was grown by the VBT growth method\textsuperscript{1}. The crystal boule was cut into sections of ~1.5 cm length and named in alphabetic order (A, B, C, …, H), where A represents the first-to-crystallize section in the pointed region of the ampoule, Supplementary Figure 1a shows single crystal specimen with cleaving along the (00\textsubscript{l}) plane, with nice flat and shiny surfaces. Supplementary Figure 1b displays a diffractogram, recorded in flat-plate reflection geometry for a single crystal specimen (Supplementary Figure 1a). The pattern contains the
diffraction peaks corresponding to only (00l) planes of very high index. The peaks are very sharp and indicate the high quality of the crystal, which is further evidenced in the very clean $K\alpha_1 - K\alpha_2$ splitting of the higher order diffraction peaks (Supplementary Figure 1c). This feature reflects the perfection of ordering of S and Te layers and the uniformity of the Sb-Bi distribution in the crystal – a non-uniform composition would broaden the peaks and the $\alpha_1-\alpha_2$ splitting would be degraded. The crystal structure was analyzed by powder X-ray diffraction on a crushed crystal, the diffraction pattern was modeled and refined using Rietveld method based on a rhombohedral cell derived from Bi$_2$Te$_{1.6}$S$_{1.4}$. The refined unit cell information, including cell parameters, atomic positions and occupancies are listed in Supplementary Table 1. The unit cell dimensions, $a = 4.21053(5)$ Å and $c = 29.5545(3)$ Å, are in good agreement with earlier reported tetradymite phases. These lattice constants are slightly different from those found for the composition Bi$_2$Te$_{1.6}$S$_{1.4}$, which has partial replacement of Te atoms in the outer layers of the quintuple layer by S atoms that leads to disorders in the quintuple layers. The atomic level lattice defects of freshly cleaved (001) surface were analyzed by recording STM topographic images (Figure 4a of main manuscript), which displayed large atomically flat regions with atomic modulations corresponding to the rhombohedral crystal structure. As expected for this type of crystal structure, the cleaving results in Te-terminated (001) surfaces. In addition to the Te atoms, the surface showed several defects.

**Supplementary Note 2 | Raman spectroscopy analysis**

The freshly cleaved (001) surface of a crystal of Sn-BSTS was subjected to analysis of its long-range lattice perfection by Raman spectroscopy. The recorded Raman spectra (Supplementary Figure 2a & b) are fit with four Lorentzians. Two of these modes are the $E_g$ and $A_{2g}$ phonons.
typically found in this range for (Bi$_{1-x}$Sb$_x$)$_2$Te$_{3-x}$Se$_x$ with the higher energy mode splitting as is typically seen for occupancy of the three X sites in the M$_2$X$_3$ quintuple layer by different ions (i.e. Te and Se or Te and S). The fourth, very broad mode is also common in these materials, and results from two-phonon scattering. The widths of the $E_g$ and $A_{2g}$ modes in Sn-BSTS (~8 cm$^{-1}$ & 11 cm$^{-1}$ respectively) are comparable with those seen in the chemically simpler material Bi$_2$Se$_3$ (~7 cm$^{-1}$ & 9 cm$^{-1}$), indicating the excellent quality of the Sn-BSTS crystal. Furthermore, the phonon positions and widths are highly reproducible from place to place in the crystal, as seen in the Supplementary Figure 2b, where we show spectra measured from three locations 2 mm apart.

**Supplementary Note 3 | Linear dispersion of surface states in the vicinity of Dirac point**

We comment on the linear dispersion of the $E$ vs. $k$ relations for the Topological Surface States in the vicinity of the Dirac point in Sn-BSTS. This is illustrated in Supplementary Figure 3. We have extracted the upper cone dispersion by using the $k$-positions (white dots in Supplementary Figure 3a) of the maximum intensity of the ARPES spectra for the potassium-deposited electron doped sample and fitted them to a line (red, slightly offset in $k$, in Supplementary Figure 3a, to reduce clutter). We then extrapolated the linear bands, and overlaid them onto an ARPES spectrum recorded at an energy that makes the lower bands visible as well. One can see from the Supplementary Figure 3b that, within a few tenths of an eV of the Dirac point and within our experimental precision, the upper and lower bands follow the same linear dispersion very well.
Supplementary Note 4 | The angular dependence of quantum oscillations

To confirm that the quantum oscillations observed in MR and Hall measurements (Figure 5a and 5b, of the main manuscript) are only from the 2-dimensional surface states, the $\rho_{xx}$ and $\rho_{yx}$ oscillations vs. inverse magnetic field were plotted for different $\theta$, the angle between applied magnetic field and current in sample (Supplementary Figures 4a and b). Both kinds of plots show a nice peak shift with $\theta$. The amplitude of oscillations gradually increased as $\theta$ approaches to 90 degrees. The angular dependent shift in the peak positions of oscillations confirms that the oscillations are only due to the 2D surface states.

Supplementary Note 5 | Low temperature synchrotron X-ray diffraction analysis

An anomalous feature is seen near 50 K in the temperature dependence of the surface conductance (Figure 6e of main manuscript text), which may either be a feature purely due to the surface state behavior, or a reflection of the presence of a structural phase transition in the underlying bulk crystal. To investigate this latter possibility, we investigated the crystal structure of Sn-BSTS in the temperature range of 2-90 K by high-resolution synchrotron powder X-ray diffraction. A plot showing the general temperature dependence of the observed diffraction patterns is shown Supplementary Figure 5a. No structural transitions are observed in this temperature range—neither in the crystal symmetry nor in the appearance of extra diffraction peaks. According to the very high resolution and high dynamic range of the synchrotron diffraction experiments, Sn-BSTS remains rhombohedral and in the tetradymite structure type to low temperatures. Further, the bulk lattice parameters ($a$ and $c$) of the rhombohedral cell can be followed at high precision as a function of $T$ from 20 K to 90 K (Supplementary Figure 5b and c). They do not exhibit any anomaly at $T \sim 50$ K. From this data it is clear that the observed
anomalies in the transport data cannot be attributed to anomalies in the structure of the underlying bulk phase. Further, the STM and APRES measurements at temperatures below 50 K did not reveal the presence of structural anomalies on the basal plane crystal surface.

Supplementary References


5. Richter, W., Becker, C. R. A Raman and far-infrared investigation of phonons in the rhombohedral V$_2$-VI$_3$ compounds Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$ and Bi$_2$(Te$_{1-x}$Se$_x$)$_3$ (0 < x < 1), (Bi$_{1-y}$Sb)$_2$Te$_3$ (0 < y < 1). *Physica Status Solidi (B)* **84**, 619 (1977).