Electronic Supplementary Information (ESI)

 Temperature-Driven n-p Conduction Type Switching without structural transition in a Cu-Rich Chalcogenide NaCu$_5$S$_3$

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Experimental section

Materials and preparation. All chemicals are commercially available and were used without further purification: NaOH (99.0%, Sinopharm Chemical Reagent Co., Ltd (SCRC)), Cu$_2$S (99.0%, Energy Chemical), Thiourea (≥99%, SCRC), and ethanediamine (≥99%, SCRC). NaCu$_5$S$_3$ polycrystals were synthesized by the solvothermal method with ethanediamine as solvent. 3.000 mmol Cu$_2$S, 4.200 mmol Thiourea (7-fold excessive stoichiometry), 84.0 mmol NaOH (70-fold excessive stoichiometry), and 6 mL of ethanediamine were loaded in a 5.6 × 7.5 inch rectangle Teflon pouch. Then, the Teflon pouches was placed in a 50 mL Teflon-lined Parr pressure vessel filled with 40 mL of deionized H$_2$O as backfill. The pressure vessels were heated to 200 °C and held for 62 h and cooled to room temperature naturally. The pouches were opened in air, and the microcrystals were washed by water and recovered by centrifugation.

Powder X-ray diffraction (XRD). To assess phase purity of the synthesized polycrystalline NaCu$_5$S$_3$ samples, powder XRD data were collected on an X’PertPW-3040 diffractometer equipped with Cu Kα radiation at room temperature. The data was recorded on a rotating anode power diffractometer operating with a voltage of 40 kV and a current of 40 mA. The simulated powder XRD pattern for comparison purpose was calculated by Mercury software.

Thermal transport measurements. Finely ground NaCu$_5$S$_3$ powder was used and the measurement was carried out with a NETZSCH 404F3 thermal analyzer. The maximum measured temperature is 400 °C with a heating/cooling rate of 10 K min$^{-1}$.
Scanning electron microscopy (SEM). JEOLJSM-6510A microscope was used to conduct SEM and energy-dispersive X-ray spectroscopy (EDS). The instrument is equipped with a PGT energy dispersive X-ray analyzer and an EDS detector.

Spark plasma sintering (SPS). Fine powdered NaCu$_5$S$_3$ sample was placed into a graphite die with 10 mm-inner diameter for SPS. SPS-1050 from Japan Sumitomo Carboniferous Co. was used for sintering. NaCu$_5$S$_3$ was sintered at 873 K and held at the highest temperature for 10 minutes under 30 MPa. The density of the sintered sample was ~95% of the theoretical density.

Electrical transport properties. The obtained cylinder was cut into bars with dimensions of ~3.0 × 4.0 × 10.0 mm$^3$ and the properties were measured perpendicular to the pressure direction. The Seebeck coefficient and electrical resistivity were measured simultaneously from room temperature to 750K under a low-pressure helium atmosphere using a commercial CRYOALL CTA-3 system. The instrument precision on the electrical resistivity and Seebeck coefficient is ~5%. For electrochemical impedance measurements, the block after the SPS was cut into pieces with a diameter of 10 mm and a thickness of 0.4 mm. AC impedance measurements were then performed using an electrochemical work station analyzer (Zennium, Zahner) at frequencies ranging from 0.1 Hz to 4 MHz.

Hall measurement. Parallelepiped-shaped samples were used for Hall measurement. The measurement was carried out using a direct current of 10 mA. The Hall coefficient ($R_H$) and the carrier concentration ($n$) were measured using a Physical Property Measurement System (PPMS 8400 series). The power factor (PF) were calculated by using the following equations:

$$PF = S^2\sigma$$

where $S$ is the Seebeck coefficient of the sample, and $\sigma$ is the electrical conductivity.

The first-principles calculations. The crystal structure of NaCu$_5$S$_3$ was employed as the initial structure model to study the cation migration within the materials. The calculations were performed by using CASTEP software (LST/QST) at the GGA level of theory. In each case, a cubic $2 \times 2 \times 2$ supercell of the simple perovskite unit cell containing 72 atoms was used to calculate the sodium migration enthalpy. Anion vacancies were generated by artificially removing one of the 48 sodium atoms within the supercell. The shortest pathway for anion ion was generated automatically from one anion site to the nearest site. During the whole calculation process, the lattice vectors of the supercell were constrained to remain cubic symmetry, but internal ionic relaxations were allowed.
**Figure S1.** Morphology of NaCu$_3$S$_3$ crystals grown from hydrothermal conditions. The element ratio of Na:Cu:S is 1.26:4.86:2.70.

**Figure S2.** Morphology of NaCu$_3$S$_3$ samples after SPS. The element ratio of Na: Cu: S is 1.35:4.77:2.88.

**Figure S3.** Optical images of the NaCu$_3$S$_3$: (a) Synthetic powder. (b, c) Sintered sample. (d) Samples cutting motif and pressure directions. (e) The cut specimens used for hall measurement. (f) The cut specimens used for electrical conductivity and seebeck coefficient tests with dimensions of ~ 3.0 × 4.0 × 10.0 mm$^3$. 
Figure S4. Repeated testing of the temperature-dependent Seebeck coefficient of NaCu₅S₃.

Figure S5. Temperature-dependent electrical conductivity of NaCu₅S₃.
Figure S6. Hall carrier mobility and Hall carrier concentration as a function of temperature.

Figure S7. Repeated testing of the temperature-dependent electrical conductivity of NaCu$_5$S$_3$.

Figure S8. DSC curves for NaCu$_5$S$_3$. 
Figure S9. TG-DTA curves for NaCu$_5$S$_3$ after SPS.

Reference