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Supplementary Information

Thermal Properties of Cubic $NaSbS_2$:Diffusion Dominant Thermal Transport Above the Debye Temperature

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Synthesis and densification of microcrystalline cubic $NaSbS_2$

Phase-pure microcrystalline cubic $NaSbS_2$ was obtained by ball milling a stoichiometric mixture of the appropriate binary compounds. Ground anhydrous Na_2S and Sb_2S_3 powder (98%, Acros Organics) were combined in a 1:1 stoichiometric ratio in a glovebox with a N_2 atmosphere. Anhydrous Na_2S was obtained by heating $Na_2S.9H_2O$ (98+%, Acros Organics) at 373 K under a dynamic vacuum for 2 days. The stainless-steel milling jars were assembled inside the glovebox with a 40:1 mass ratio of stainless-steel milling balls to powder. Ball milling was carried out using a gear drive 4-station planetary ball mill (Acros International, model no.: PQ-N2) at 425 rpm for 6 h. Densification of the microcrystalline powder was carried out using Spark Plasma Sintering (SPS, Thermal Technology Model 10-3). The specimen was loaded into a custom designed tungsten carbide punch and die assembly lined with graphite foil to prevent reaction with surrounding material. SPS densification was carried out under vacuum at 400 MPa and 423 K. The temperature ramp rate was 25 K/min. The pressure and current were maintained for 15 minutes once the desired temperature was reached. The resulting densified pellet had a relative density of 90%.

Crystal structure refinement

Rietveld structure refinement of X-ray diffraction (XRD) measurements was employed to analyze the crystal structure of cubic $NaSbS_2$. Powder XRD data were collected with a Bruker-AXS D8 Focus diffractometer in Bragg–Brentano geometry with Cu Kα radiation and a graphite monochromator. Rietveld refinement was performed using GSAS II software[1]. The initial parameters for structure refinement were based on structural data previously reported[2].

Electrical and thermal properties measurements

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) under nitrogen gas flow for the as-synthesized powder were performed using a TA Instruments Q600 apparatus. A 2 x 2 x 5 mm^3 parallelepiped was cut from the densified pellet using a wire saw for low temperature steady state κ measurements. A custom designed radiation shielded vacuum probe[3,4] was used to measure κ from 30 K to 300 K with 8% maximum experimental uncertainty. The heat capacity (HC) option of the physical property measurement system (PPMS) from Quantum Design was utilized for C_p measurements. Thermal N-grease was used to couple the specimen with the mounting stage of the HC module. The measurements were performed from 300 K to 2 K involving a 2% temperature rise. The two-tau model of the Quantum Design heat capacity software was used for the measurements. Appropriate addendum measurements accompanied the sample C_p measurements. Room temperature four-point probe resistivity measurements were conducted for a 2 x 2 x 5 mm^3 specimen using the resistivity option of the PPMS.

Table S1. Summary of Rietveld refinement results.

Compound	$Na_{0.5}Sb_{0.5}S$
crystal system	cubic
space group	$Fm\bar{3}m$ (#225)
a (Å)	5.7678 (9)
V (Å^3)	191.88 (9)
Z	4
mol. w. (g/mol)	104.43
d_{calc} (g/cm^3)	3.615
Radiation	Graphite monochromated
	Cu Kα (1.5406 Å)
2θ range (^{o})	20 - 100
wRp, Rp	0.06868, 0.05415
GOF	1.130

Table S2. Atomic coordinates, fractional occupancy, and isotropic atomic displacement parameters.

Atom	Site	x	y	z	Atomic Occupancy	U_{iso} (Å^2)
Na	4a	0	0	0	0.5	0.01 (20)
Sb	4a	0	0	0	0.5	0.01 (5)
S	4b	1/2	1/2	1/2	1	0.026 (6)

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