

Supplementary Materials

Random aliovalent cations induce synergistic bonding for high thermoelectric performance in NaSn₂SbSe₄

Yanting Qin¹, Qingzhi Song¹, Linyu Bai¹, Qingshan Bao¹, Xiufeng Cheng¹, Lili Li¹, Yanlu Li¹, Xian Zhao²

¹State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, Shandong, China.

²Center for Optics Research and Engineering, Shandong University, Qingdao 266237, Shandong, China.

Correspondence to: Dr. Lili Li, Prof. Yanlu Li, State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, Shandong, China. E-mail: lili.li@sdu.edu.cn; liyanlu@sdu.edu.cn

1. Calculation principle of partial parameters

1.1 Thermal Transport Properties

The thermal transport parameters are obtained using the phonon Boltzmann transport equation (BTE), implemented in the FourPhonon package^[1], and the lattice thermal conductivity (κ_L) is computed as follows^[2, 3]:

$$\kappa_L = \frac{\hbar^2}{k_B T^2 V N_q} \sum_{q,v} n_{qv} (\mathbf{n}_{qv} + \mathbf{1}) \omega_{qv}^2 v_{qv} F_{qv} \quad (1)$$

Where \hbar is the reduced Planck's constant, k_B is the Boltzmann constant, V is the volume of the unit cell, and N_q is the number of wave vectors. q and v serve as indices for phonon modes. ω_{qv} represents the phonon frequency, and v_{qv} is the group velocity. Moreover, F_{qv} is associated with the phonon lifetime, characterizing the influence of phonon scattering processes on κ_L .

1.2 Electronic Transport Properties

To accurately model cation disorder, a $2 \times 2 \times 2$ supercell containing 64 atoms (8 Na, 8 Sb, 16 Sn, and 32 Se atoms) was built for electronic transport properties, as shown in Figure S5^[4]. The optimized lattice parameters are $a = b = c = 12.09 \text{ \AA}$.

Within the framework of Boltzmann transport theory under the relaxation time approximation (RTA), the electrical conductivity (σ) and Seebeck coefficient (S) are formulated as^[5, 6]:

$$\sigma = e^2 \int \sum_k v_k v_k \tau_k \left(-\frac{\partial f_0}{\partial \varepsilon} \right) d\varepsilon \quad (2)$$

$$S = \frac{e k_B}{\sigma} \int \sum_k v_k v_k \tau_k \frac{\varepsilon - \mu}{k_B T} \left(-\frac{\partial f_0}{\partial \varepsilon} \right) d\varepsilon \quad (3)$$

Where e , f_0 , ε , k_B , and μ represent the electron charge, Fermi-Dirac distribution function, energy eigenvalue, Boltzmann constant, and chemical potential, respectively. Similarly, τ_k and v_k denote the relaxation time and group velocity associated with wave vector k , respectively.

By utilizing deformation potential (DP) theory, the relaxation times (τ) are calculated by using the following equation^[7-9].

$$\tau = \frac{2\sqrt{2}\pi C^{3D} \hbar^4}{3(k_B T m^*)^2 E_1^2} \quad (4)$$

Where C^{3D} , \hbar , m^* , and E_1 are the elastic constant, reduced Planck constant, charge effective mass, and the energy change in the valence band, respectively. According to the Wiedemann-Franz law, the electronic thermal conductivity (κ_e) can be evaluated as^[10]:

$$\kappa_e = L \sigma T \quad (5)$$

Where L represents the Lorenz number. In general, the formula can be written as $L = 1.5 + \exp(-|S|/116)$ for $\text{NaSn}_2\text{SbSe}_4$. Additionally, because the experimental Seebeck coefficient and electrical conductivity are unavailable, we adopt $L = 2.48 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ for SnSe ^[11].

2. Supporting figures

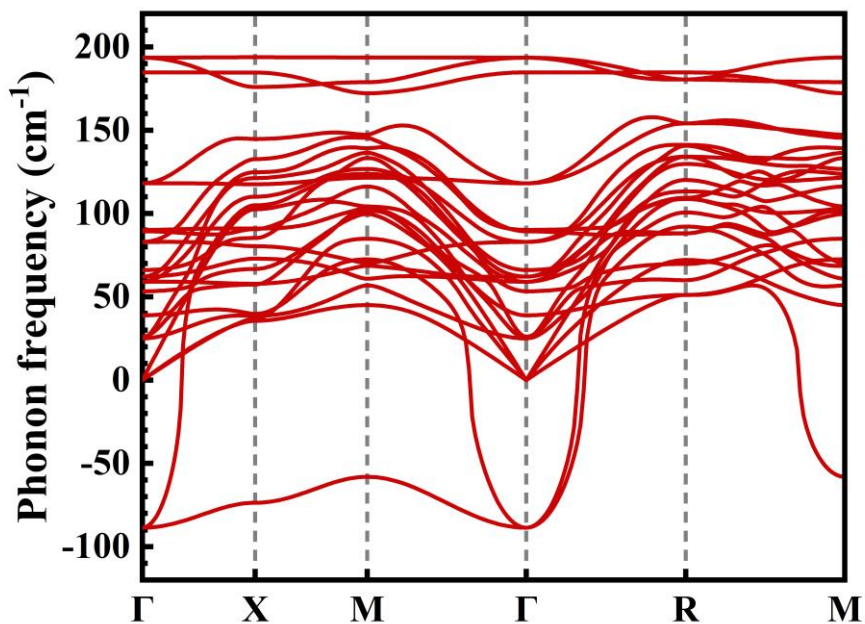


Figure S1. Harmonic phonon dispersion of NaSn₂SbSe₄ calculated at 0 K.

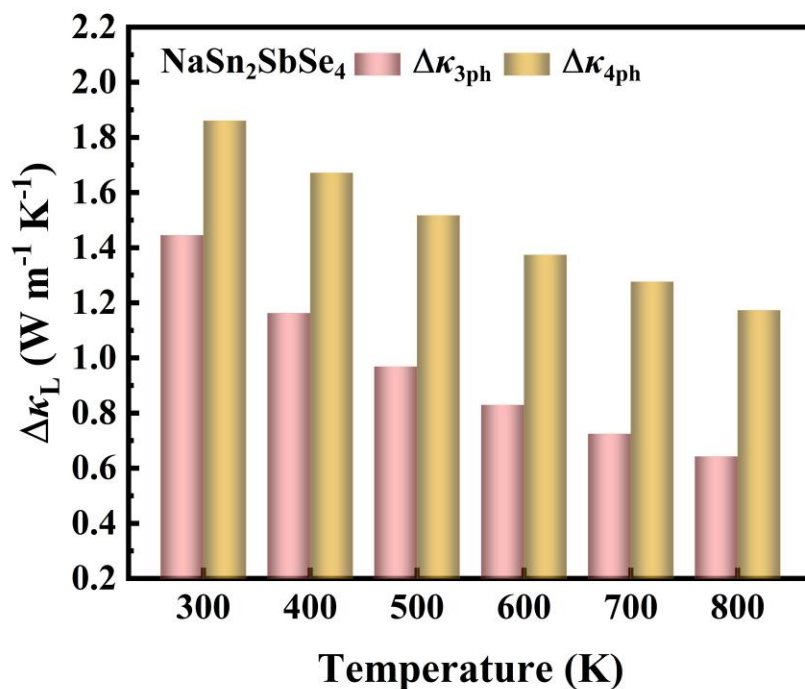


Figure S2. Comparison of the reduction in lattice thermal conductivity (κ_L) of NaSn₂SbSe₄ induced by three- and four-phonon scattering.

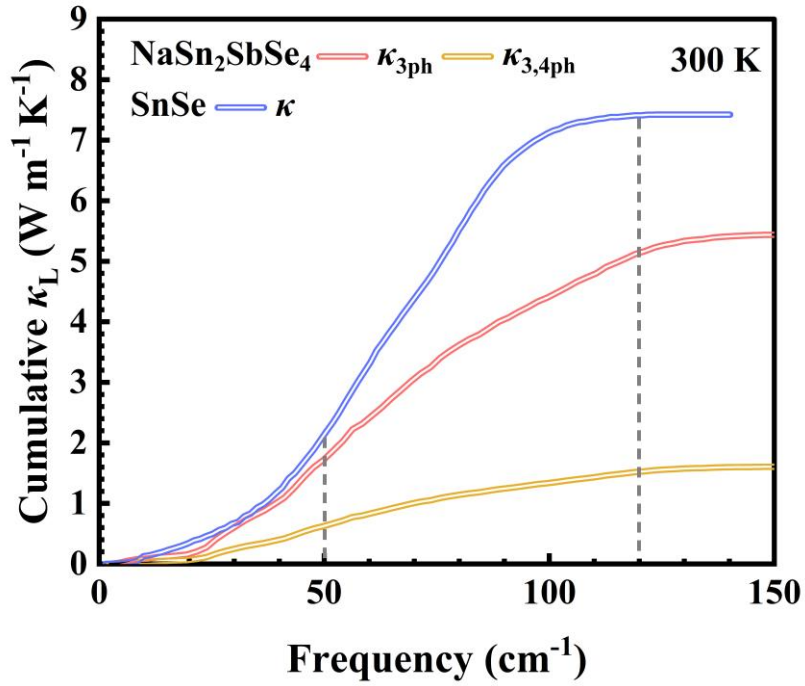


Figure S3. Calculated phonon frequency-dependent cumulative lattice thermal conductivity at 300 K for SnSe and NaSn₂SbSe₄.

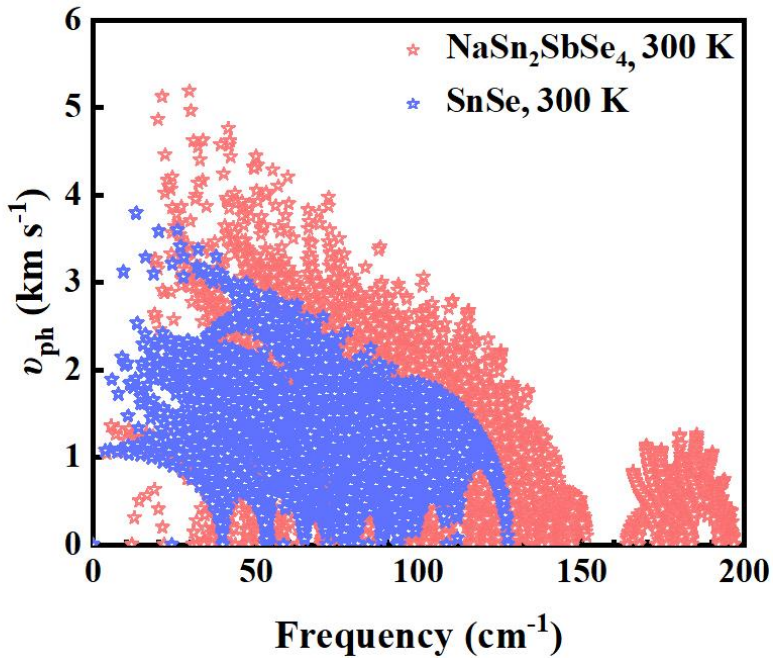


Figure S4. Calculated phonon group velocity (v_{ph}) at 300 K for SnSe and NaSn₂SbSe₄.

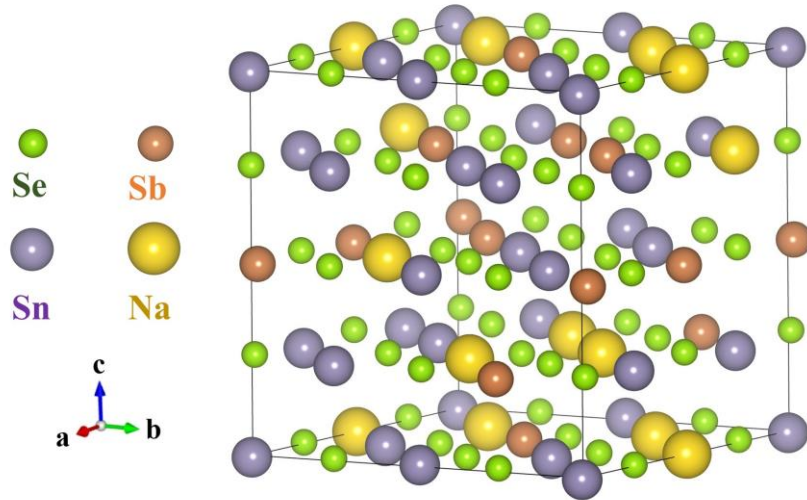


Figure S5. Structure of special quasi-random structure (SQS) for $\text{NaSn}_2\text{SbSe}_4$.

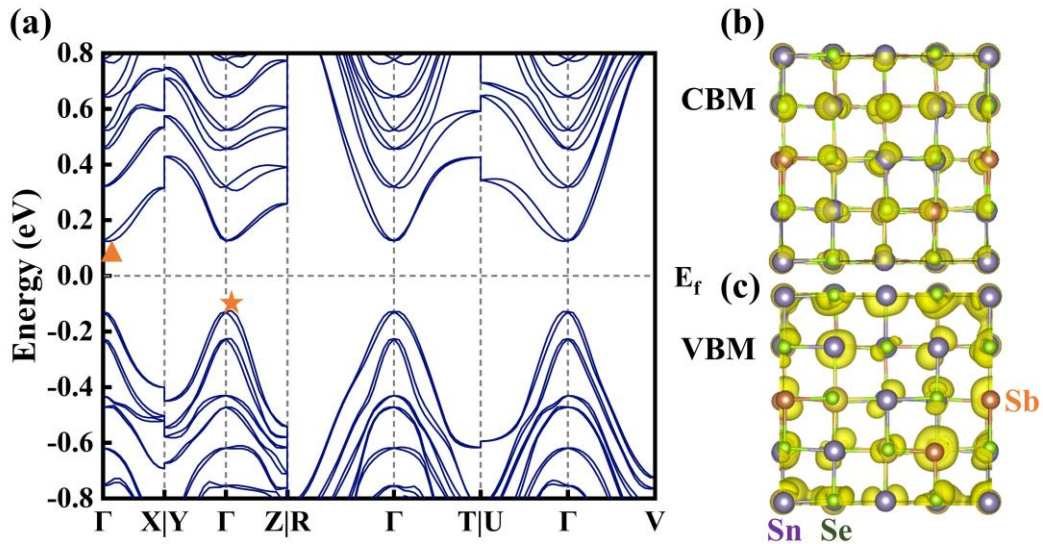


Figure S6. (a) Calculated electronic band structure of $\text{NaSn}_2\text{SbSe}_4$ with SOC. The Fermi level is set to 0 eV. The corresponding charge densities at (b) conduction band minimum (CBM) and (c) valence band maximum (VBM) in the b-c plane. An isosurface with a constant charge density of $2 \times 10^{-5} \text{ e}\text{\AA}^{-3}$ ($2 \times 10^{-4} \text{ e}\text{\AA}^{-3}$) is used to present the contour of charge density.

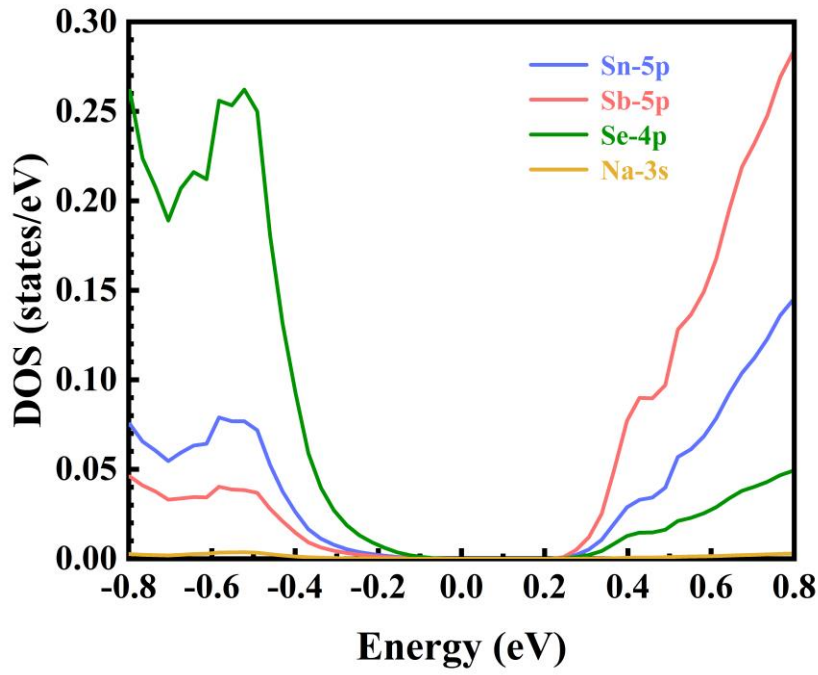


Figure S7. Calculated projected density of states (PDOS) of $\text{NaSn}_2\text{SbSe}_4$.

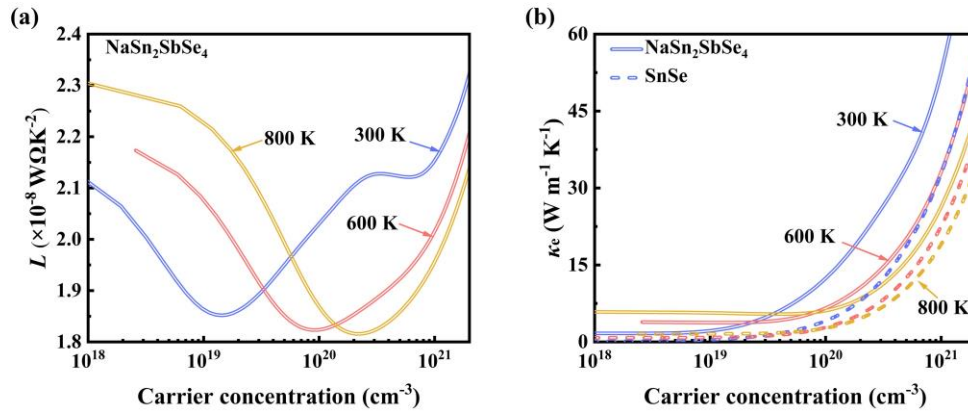


Figure S8. (a) Calculated Lorenz numbers of $\text{NaSn}_2\text{SbSe}_4$, and (b) electronic thermal conductivities (κ_e) of SnSe and $\text{NaSn}_2\text{SbSe}_4$ as a function of carrier concentration.

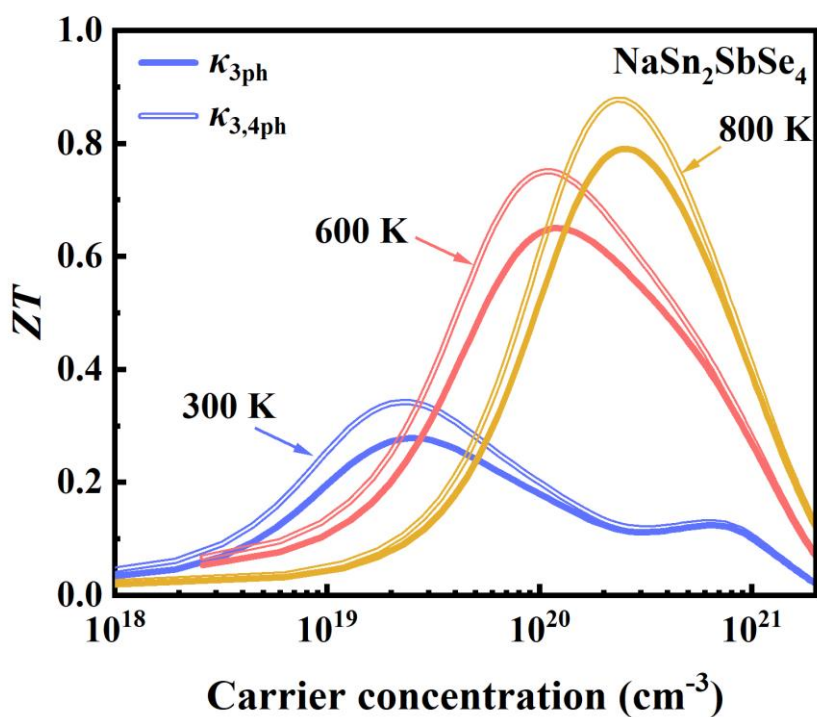


Figure S9. Calculated ZT values for $\text{NaSn}_2\text{SbSe}_4$ with $\kappa_{3\text{ph}}$ and $\kappa_{3,4\text{ph}}$ at 300, 600, and 800 K.

3. Supporting tables

Table S1. Optimized lattice parameters of $\text{NaSn}_2\text{SbSe}_4$ and SnSe , along with the corresponding lattice parameter change rates relative to SnSe

Lattice parameters							lattice parameter change rates	
	a	b	c	α	β	γ	a	b/c
SnSe	6.053Å	6.053Å	6.053Å	90°	90°	90°		
$\text{NaSn}_2\text{SbSe}_4$	5.954Å	5.931Å	5.931Å	90°	90°	90°	1.636%	2.016%

Table S2. The Sn–Se bond lengths (Å) along the a , b , and c -axes in SnSe and Sb/Na/Sn–Se bond lengths in NaSn₂SbSe₄ for the corresponding atomic configurations. Degree of bond length distortion relative to SnSe

Bond length (Å)		Degree of distortion				
		a -axis	b -axis	c -axis	a -axis	b/c -axis
SnSe	Sn-Se	3.026	3.026	3.026		
	Sb-Se	2.977	2.965	2.965	1.619%	2.016%
NaSn ₂ SbSe ₄	Na-Se	2.977	2.965	2.965	1.619%	2.016%
	Sn-Se	2.977	2.965	2.965	1.619%	2.016%

Table S3. Diagonal element of optical dielectric constant for SnSe and NaSn₂SbSe₄

Optical dielectric constant	xx	yy	zz
SnSe	76.79	76.79	76.79
NaSn ₂ SbSe ₄	320.00	284.48	284.48

Table S4. Calculated charge effective mass m^* (m_e), elastic constant C^{3D} (eV/Å³), DP constant E_I , and the relaxation time τ (ps) for SnSe and NaSn₂SbSe₄

Carrier type		m^* (m_e)	C^{3D} (eV/Å ³)	E_I (eV)	τ (ps)
NaSn ₂ SbSe ₄	Hole	0.2	0.42	8.16	0.3947 (300 K)
					0.1395 (600 K)
					0.0906 (800 K)
SnSe	Hole	0.58	0.77	12.59	0.0646 (300 K)
					0.0214 (600 K)
					0.0139 (800 K)

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