

Thermoelectric Zintl phases with ultralow thermal conductivity. Synthesis, structural characterization, and transport properties of $\text{Ca}_{10}\text{AlSb}_9$ and $\text{Ca}_{10}\text{CdSb}_9$

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CONTENTS

Figure S1. Powder X-ray diffraction patterns for as-synthesized powder samples of $\text{Ca}_{10}\text{CdSb}_9$ and $\text{Ca}_{10}\text{AlSb}_9$.

Figure S2. Representation of the $[\text{AlSb}_4]$ and $[\text{Ca}_4\text{Sb}_6]$ polyhedra in $\text{Ca}_{10}\text{AlSb}_9$, showing their “overlapping”.

Figure S3. Total and projected electronic density of state (DOS) for $\text{Ca}_{11}\text{CdSb}_9$ model.

Figure S4. Schematic representation for the structural disorder in $\text{Ca}_{11}\text{CdSb}_9$ (model III). Respective occupancies are annotated.

Figure S5. Thermoelectric quality factor for $\text{Ca}_{11}\text{CdSb}_9$.

Table S1. Selected distances in $\text{Ca}_{10}\text{AlSb}_9$.

Table S2. Selected distances in $\text{Ca}_{10}\text{CdSb}_9$.

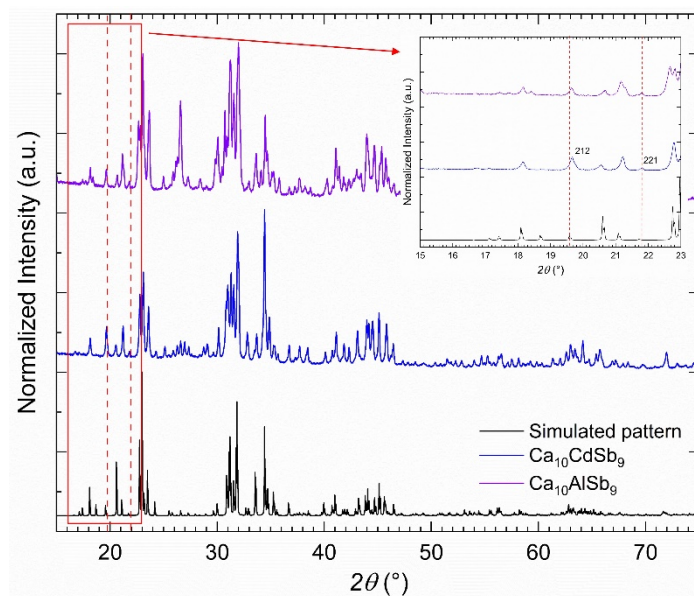


Figure S1. Powder X-ray diffraction patterns for as-synthesized powder samples of $\text{Ca}_{10}\text{CdSb}_9$ and $\text{Ca}_{10}\text{AlSb}_9$. The inset shows the magnified range of 2θ from 15° to 23° , where the vertical red dashed line shows the Bragg reflections (212) and (221) at 2θ of 19.9° and 22° .

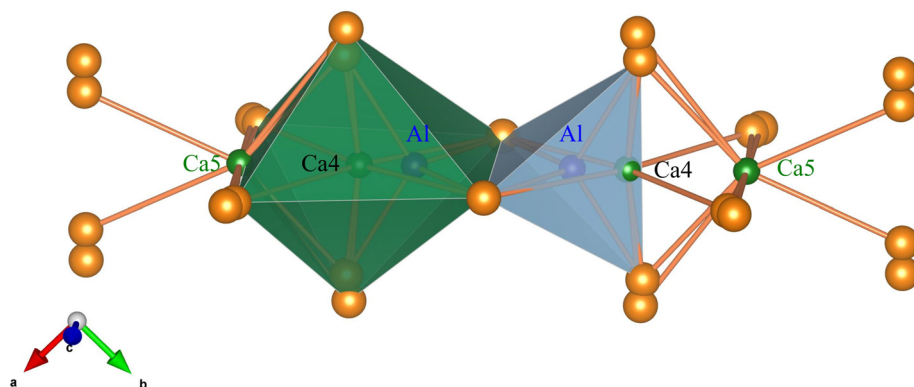


Figure S2. Representation of the $[\text{AlSb}_4]$ and $[\text{Ca}_4\text{Sb}_6]$ polyhedra in $\text{Ca}_{10}\text{AlSb}_9$, showing their “overlapping”. One can see the Al atom lie inside the $[\text{Ca}_4\text{Sb}_6]$ octahedra indicating that these two polyhedra cannot exist simultaneously.

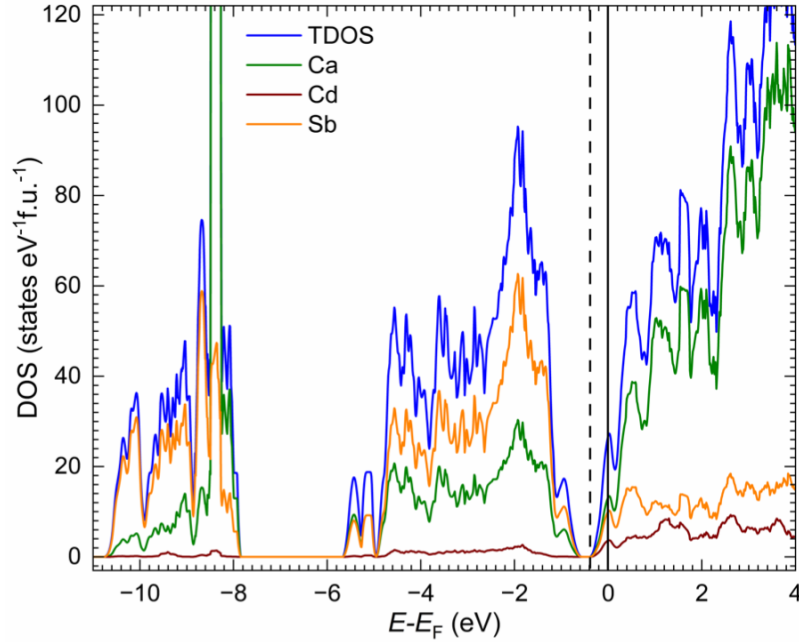


Figure S3. Total and projected electronic density of state (DOS) for $\text{Ca}_{11}\text{CdSb}_9$ model. The vertical solid line indicates the Fermi level while the vertical dashed line close to the solid line represents the actual Fermi level position after removing one electron per formula unit.

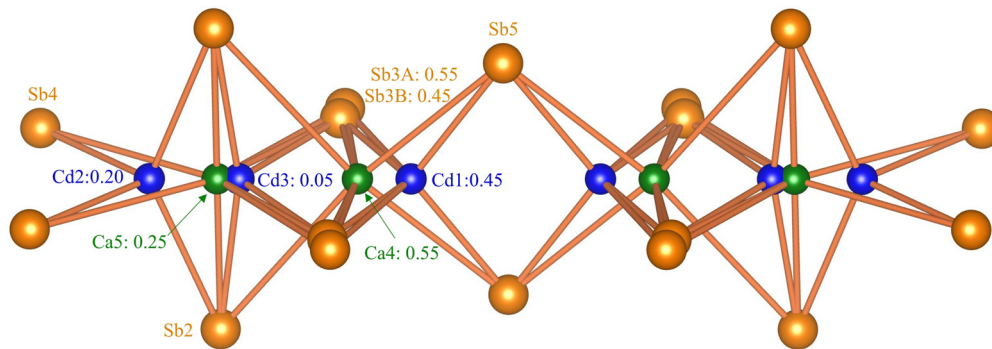


Figure S4. Schematic representation for the structural disorder in $\text{Ca}_{11}\text{CdSb}_9$ (model III). Respective occupancies are annotated.

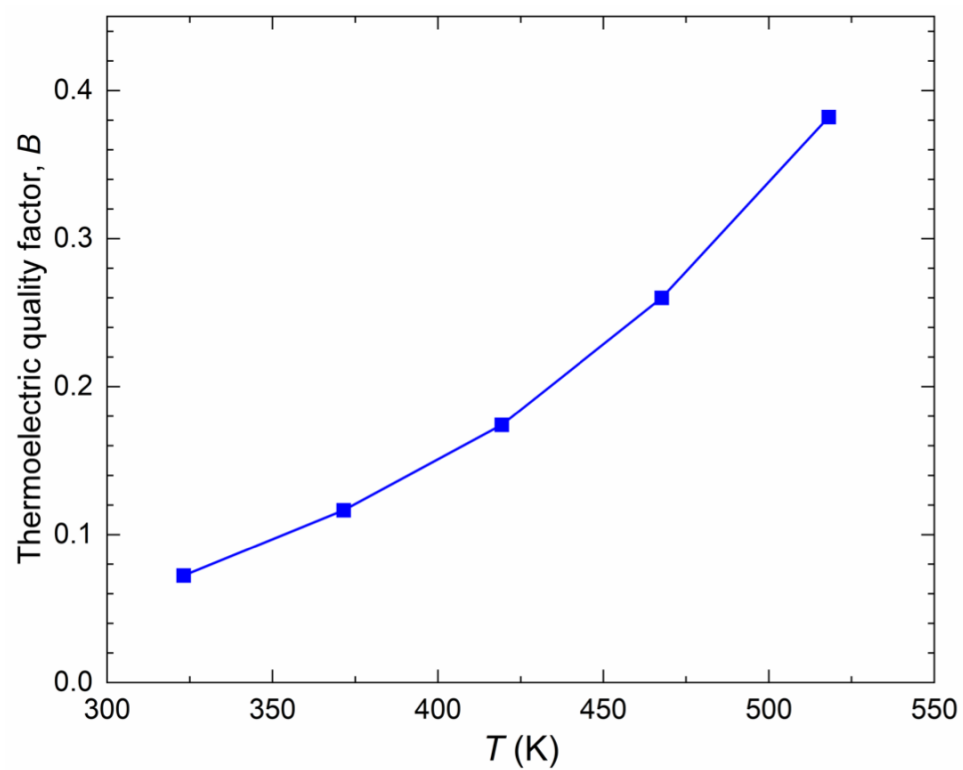


Figure S5. Thermoelectric quality factor for $\text{Ca}_{11}\text{CdSb}_9$.

Table S1. Selected distances in Ca₁₀AlSb₉.

	Atoms	Distances (Å)		Atoms	Distances (Å)	
Ca1	Sb6	3.140(1)	Ca5	Sb2A ×2	2.864(1)	
	Sb5	3.175(1)		Sb2B ×2	3.079(1)	
	Sb2B	3.294(1)		Sb3B ×2	3.201(1)	
	Sb3B	3.379(1)		Sb4B ×2	3.51(1)	
	Sb1	3.385(1)		Sb3A ×2	3.661(1)	
	Sb1	3.438(1)		Sb4A ×2	3.834(6)	
	Sb3A	3.458(1)				
	Sb2A	3.528(1)		Ca6A	Sb4B ×2	2.816(5)
	Sb2A	3.589(1)			Sb2B ×2	3.151(4)
		Sb4A ×2	3.207(3)			
Ca2	Sb1	3.139(1)		Sb2A ×2	3.359(2)	
	Sb3A	3.139(1)		Sb1 ×2	3.770(1)	
	Sb6	3.179(1)	Ca6B	Sb2B ×2	3.093(4)	
	Sb2A	3.184(2)		Sb4B ×2	3.13(1)	
	Sb3A	3.214(1)		Sb2A ×2	3.328(2)	
	Sb3B	3.220(2)		Sb4A ×2	3.49(1)	
	Sb2B	3.228(1)		Sb5	3.63(4)	
	Sb4A	3.359(1)		Sb1 ×2	3.717(1)	
Ca3A	Sb3A	3.007(2)	Al1	Sb5 ×2	2.721(4)	
	Sb3A	3.008(2)		Sb3B ×2	2.761(7)	
	Sb3B	3.130(3)		Sb3A ×2	3.221(7)	
	Sb3B	3.130(3)	Sb1	Sb2B	2.892(6)	
	Sb4A	3.278(2)		Sb2A	2.947(3)	
Ca3B	Sb3A	3.06(5)	Ca3A	Ca3B ×2	0.67(5) ^a	
	Sb3A	3.06(5)		Ca4	Al1	1.142(8) ^a
	Sb3B	3.06(5)	Ca5		2.464(7) ^a	
	Sb3B	3.06(5)				
	Sb5	3.20(3)				
Ca4	Sb3B ×2	2.375(4)				
	Sb3A ×2	2.919(4)				
	Sb5 ×2	3.523(3)				
	Ca3B ×2	3.62(5)				
	Sb2A ×2	3.687(3)				

^a Unphysical distances between partial occupied sites.

Table S2: Selected distances in Ca₁₀CdSb₉.

	Atoms	Distances (Å)		Atoms	Distances (Å)
Ca1	-Sb6	3.1399(9)	Ca5	-Sb2 ×2	2.974(1)
	-Sb5	3.153(1)		-Sb3B ×2	3.182(6)
	-Sb3B	3.397(1)		-Sb3A ×2	3.556(5)
	-Sb1	3.401(0)		-Sb4 ×2	3.977(5)
	-Sb3A	3.461(2)	Ca6	-Sb2 ×2	3.2740(4)
	-Sb1	3.463(1)		-Cd2 ×2	3.351(2)
	-Sb2	3.466(1)		-Sb4 ×2	3.381(2)
Ca2	-Sb3A	3.135(2)	Cd1	-Sb5 ×2	2.846(1)
	-Sb1	3.139(1)		-Sb3B ×2	2.862(3)
	-Sb6	3.179(1)		-Sb3A ×2	3.207(2)
	-Sb3B	3.184(2)	Cd2	-Sb4 ×2	2.924(2)
	-Sb2	3.207(1)		-Sb2 ×2	3.214(1)
	-Sb3A	3.211(2)		Sb1	-Sb2
	-Sb4	3.386(1)	Sb3A		-Sb3B
	-Sb3B	3.491(3)	Ca4	-Cd1	0.961(4) ^a
Ca3	-Sb3A	3.011(3)		-Ca5	2.384(6) ^a
	-Sb3B	3.122(4)	Ca5	-Cd2	1.334(5) ^a
	-Sb4	3.301(1)			
Ca4	-Sb3B ×2	2.541(5)			
	-Sb3A ×2	2.946(4)			
	-Sb5 ×2	3.504(3)			

^a Unphysical distances between partial occupied sites.