SUPPLEMENTARY INFORMATION

A novel crystallographic location of rattling atoms in filled $Eu_xCo_4Sb_{12}$ skutterudites prepared under high-pressure conditions

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Table S1. Crystallographic parameters for $Eu_xCo_4Sb_{12}$ prepared under high-pressure conditions, refined from SXRD data at 473 K.

Crystal data

Cubic, $Im\bar{3}$	SXRD, λ= 0.45861 Å
a = 9.05127(2) Å	V = 741.53(1) Å^3
Z = 2	

Refinement

R_p = 11.36%	R_{wp} = 19.59%
R_{exp} = 5.57%	R_{Bragg} = 2.40%
χ^2 = 5.39	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	Site	*x*	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co	8*c*	1/4	1/4	1/4	0.0085(4)	
Sb	24*g*	0	0.33483(6)	0.15793(6)	0.0107(4)	0.992(4)
Eu	12*d*	0.25(3)	0	0	0.02533*	0.0026(12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0085(4)	0.0085(4)	0.0085(4)	0.0003(5)	0.0003(5)	0.0003(5)
Sb	0.0088(3)	0.0128(4)	0.0106(4)	0.00000	0.00000	0.0010(3)

Table S2. Crystallographic parameters for $Eu_xCo_4Sb_{12}$ prepared under high-pressure conditions, refined from SXRD data at 673 K.

Crystal data

Cubic, $Im\bar{3}$	SXRD, λ= 0.45861 Å
a = 9.069007(19) Å	V = 745.90(1) Å^3
Z = 2	

Refinement

R_p = 10.75%	R_{wp} = 19.30%
R_{exp} = 5.57%	R_{Bragg} = 2.40%
χ^2 = 4.95	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Co	1/4	1/4	1/4	0.0112(4)	
Sb	0	0.33469(6)	0.15792(7)	0.0141(4)	0.985(4)
Eu	0.24(3)	0	0	0.03800*	0.0024(12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0112(4)	0.0112(4)	0.0112(4)	0.0012(5)	0.0012(5)	0.0012(5)
Sb	0.0111(3)	0.0175(4)	0.0138(4)	0.00000	0.00000	0.0015(3)

Table S3. Crystallographic parameters for $Eu_xCo_4Sb_{12}$ prepared under high-pressure conditions, refined from SXRD data at 873 K.

Crystal data

Cubic, $Im\bar{3}$	SXRD, λ= 0.45861 Å
a = 9.08701(2) Å	V = 750.35(1) Å^3
Z = 2	

Refinement

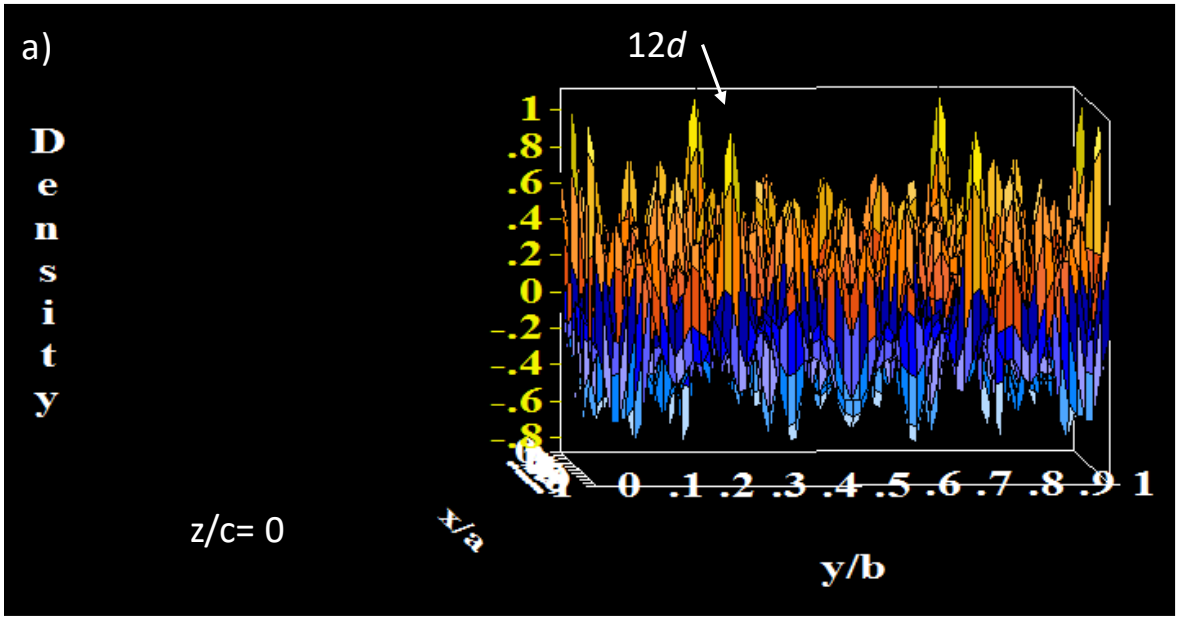
R_p = 13.44%	R_{wp} = 24.57%
R_{exp} = 5.59%	R_{Bragg} = 3.14%
χ^2 = 5.76	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Co	1/4	1/4	1/4	0.0140(5)	
Sb	0	0.33445(8)	0.15792(8)	0.0187(5)	0.985(4)
Eu	0.24000	0	0	0.03800*	-0.0014(14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0140(5)	0.0140(5)	0.0140(5)	0.0009(6)	0.0009(6)	0.0009(6)
Sb	0.0146(4)	0.0236(5)	0.0180(5)	0.00000	0.00000	0.0023(3)



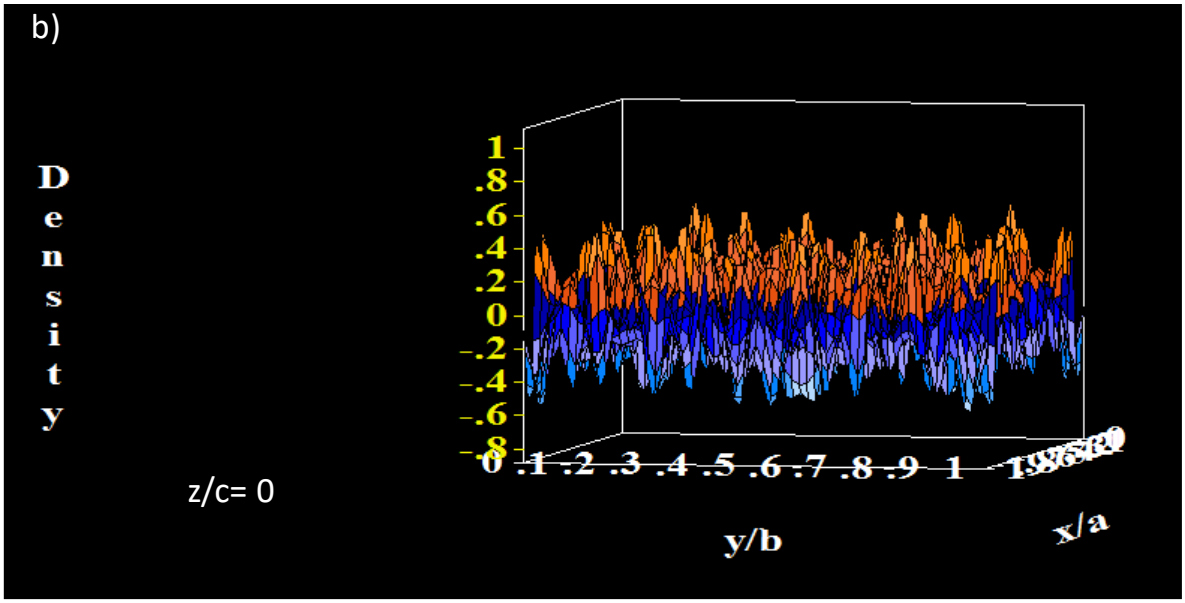


Figure S1. Two Fourier difference plots for z = 0, **(a)** before and **(b)** after the introduction of Eu at 12*d* positions.

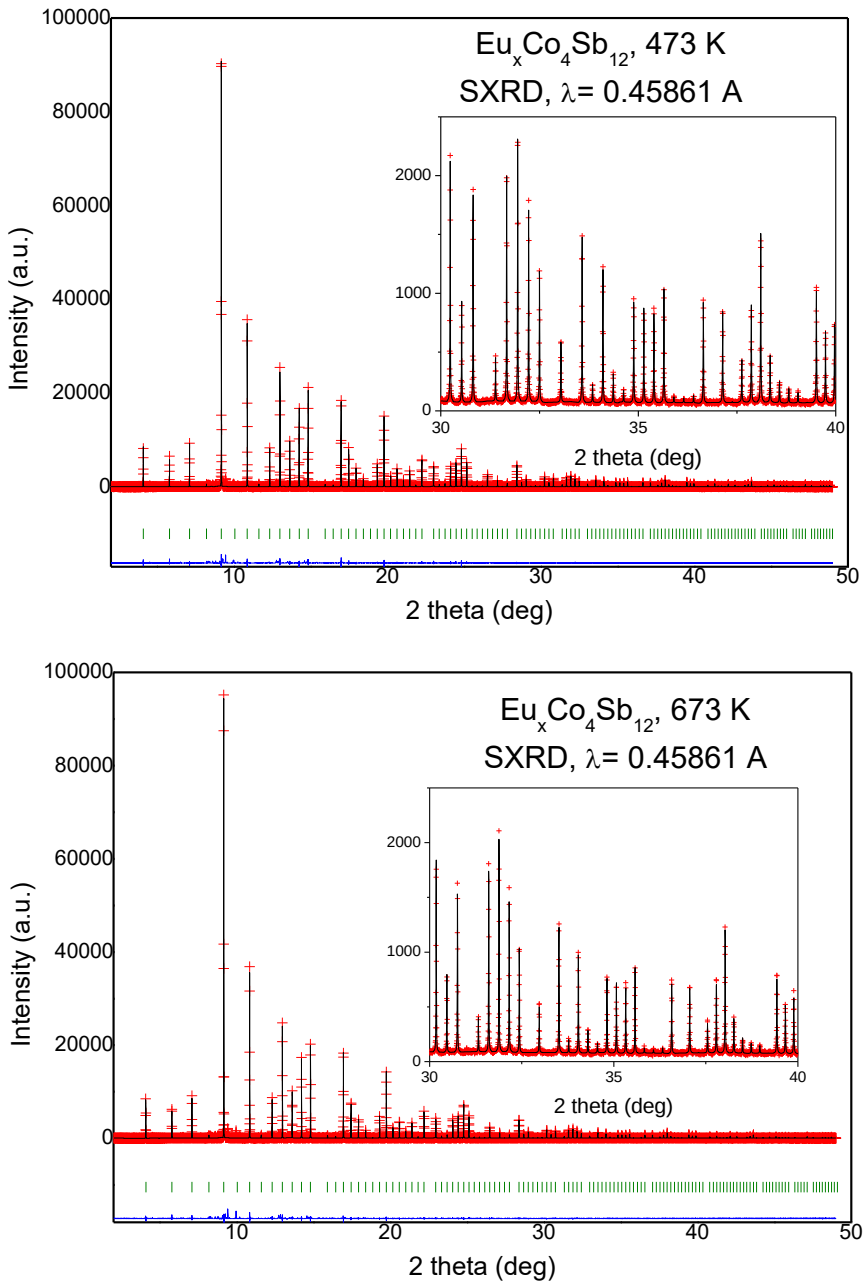


Figure S2. Observed (red crosses), calculated profile (black line), difference (blue line) and Bragg reflections (green symbols) SXRD pattern for $Eu_xCo_4Sb_{12}$ at **(a)** 473 K and **(b)** 673 K. The insets show the quality of the fits in the high-angle region.

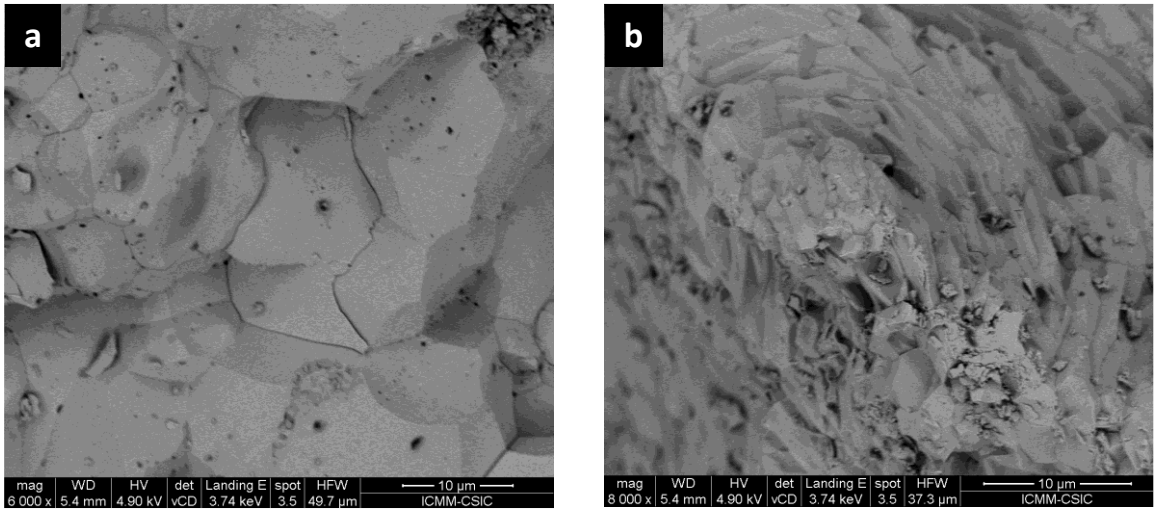


Figure S3. Additional SEM micrographs of the as-grown pellets of $Eu_{0.02(1)}Co_4Sb_{12}$. **(a)** x6000 and **(b)** x8000 magnification.

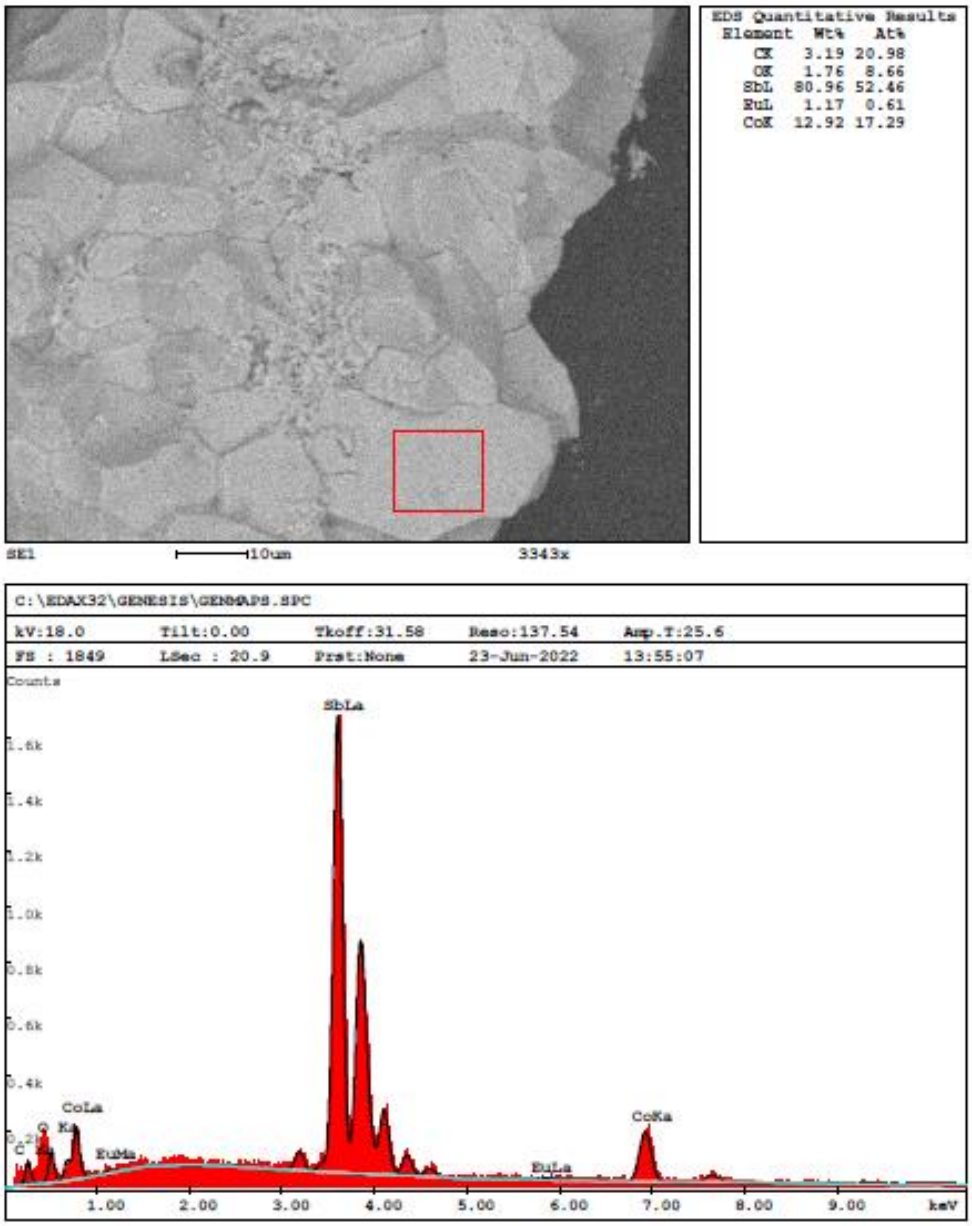


Figure S4. Upper panel: SEM image where the EDX spectrum was collected, and relative contents of Sb, Co, and Eu. Lower panel: typical EDX spectrum.

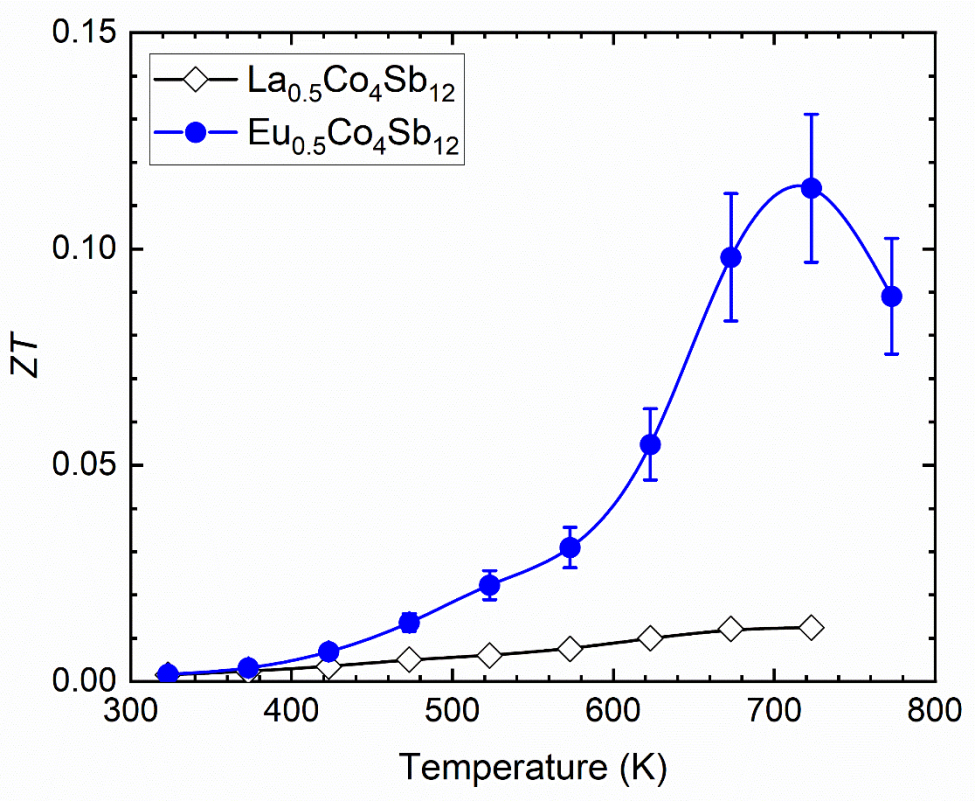


Figure S5. Thermoelectric figure of merit (ZT) as a function of temperature for the $Eu_{0.5}Co_4Sb_{12}$ compound, and $La_{0.5}Co_4Sb_{12}$ synthesized under high-pressure. Both compositions refer to their nominal chemical formula.