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Electronic Supplementary Information

Low Thermal Conductivity in La-Filled Cobalt Antimonide Skutterudites with Inhomogeneous Filling Factor Prepared Under High-Pressure Conditions

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Synchrotron Rietveld refinements

Table ESI.1. Structural parameters of $La_{0.5}Co_4Sb_{12}$ at different temperatures from Rietveld refinement. Space group: $Im\bar{3}$

Temperature (K)	**473**		**673**		**873**		**1073**	
phase	$La_{0.17}Co_4Sb_{11.64}$	$La_{0.052}Co_4Sb_{11.68}$	$La_{0.17}Co_4Sb_{11.64}$	$La_{0.052}Co_4Sb_{11.68}$	$La_{0.17}Co_4Sb_{11.64}$	$La_{0.052}Co_4Sb_{11.68}$	$La_{0.17}Co_4Sb_{11.64}$	$La_{0.052}Co_4Sb_{11.68}$
Lattice parameter, *a* / Å	9.07051(1)	9.05589(5)	9.089329	9.073526	9.106850	9.090670	9.124289	9.109952
y (Sb)	0.3350(5)		0.33511		0.33493		0.33465	
z (Sb)	0.1581(5)		0.15823		0.15813		0.15816	
U_{11} (Co) / Å^2 *	0.0093(4)		0.0122(5)		0.0163(5)		0.0209(9)	
U_{12} (Co) / Å^2 **	0.0006(7)		0.0007(9)		0.0004(8)		0.0008(15)	
U_{11} (Sb) / Å^2 ***	0.0102(5)		0.0133(6)		0.0167(5)		0.0226(9)	
U_{22} (Sb) / Å^2	0.0160(7)		0.0216(8)		0.0293(8)		0.0342(15)	
U_{33} (Sb) / Å^2	0.0115(6)		0.0171(8)		0.0211(7)		0.0273(12)	
U_{23} (Sb) / Å^2	0.0016(4)		0.0022(5)		0.0024(4)		0.0026(9)	
U_{11} (La) / Å^2 ****	0.016(4)		0.035(7)		0.047(7)		0.047(12)	
R_p (%)	5.94		6.30		5.84		6.95	
R_{wp} (%)	7.42		8.56		7.31		12.3	
R_{exp} (%)	5.93		5.92		5.93		6.02	
χ^2 (%)	1.57		2.09		1.52		4.15	
R_I	1.77	1.88	2.14	2.65	2.10	1.88	3.77	3.49

Sb at 24*g*, (*0*,*y*,*z*); Co at 8*c* (¼,¼,¼); La at 2a (0,0,0)

*Anisotropic Ux10⁴ Co:** $U_{11} = U_{22} = U_{33}$;** $U_{12} = U_{23} = U_{13}$; Sb:*** $U_{12} = U_{13} = 0$; La:**** $U_{11} = U_{22} = U_{33}$

Figure ESI.1. Synchrotron XRD profiles of $La_{0.5}Co_4Sb_{12}$ at different temperatures. Observed (red crosses), calculated (black solid line), and difference (blue line at the bottom). Allowed Bragg reflections are indicated by the green tick marks. The onset of decomposition of the material is observed at 1073 K as additional reflections.

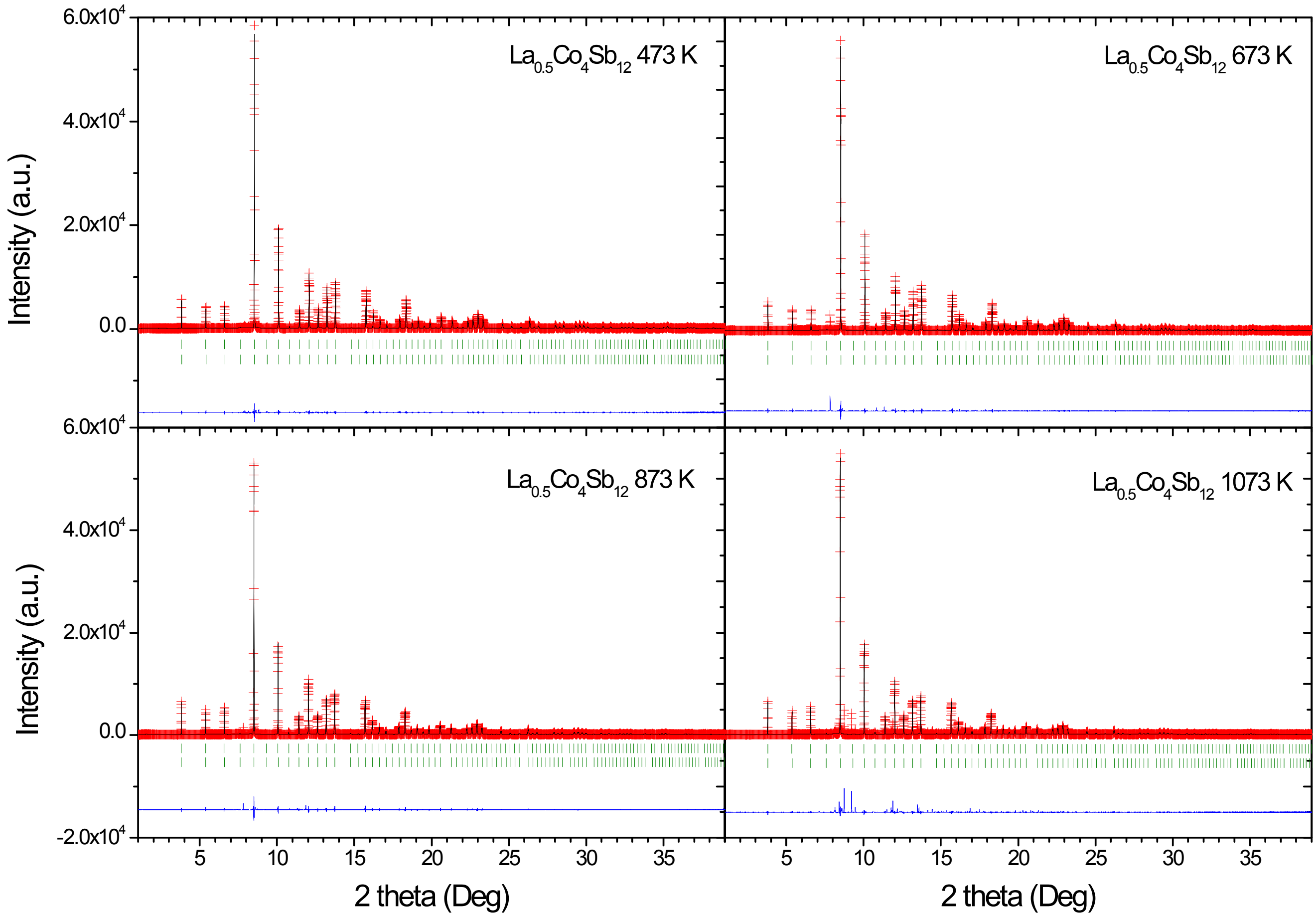


Figure ESI.2. Observed (red crosses), calculated (black full line) and difference (blue line) laboratory (Cu Kα) XRD profiles for $La_{0.25}Co_4Sb_{12}$ at room temperature. Inset: close up of the high-angle region showing the splitting of all reflections due to Kα1 and Kα2 radiation. The resolution in not sufficient to discern the presence of two perovskite phases, only distinguishable from SXRD data.

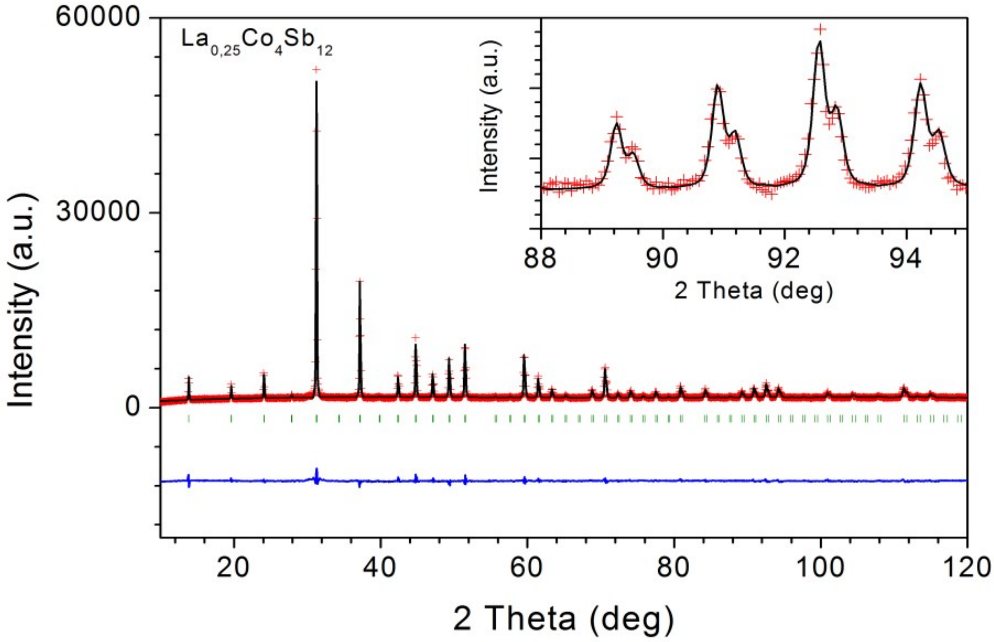
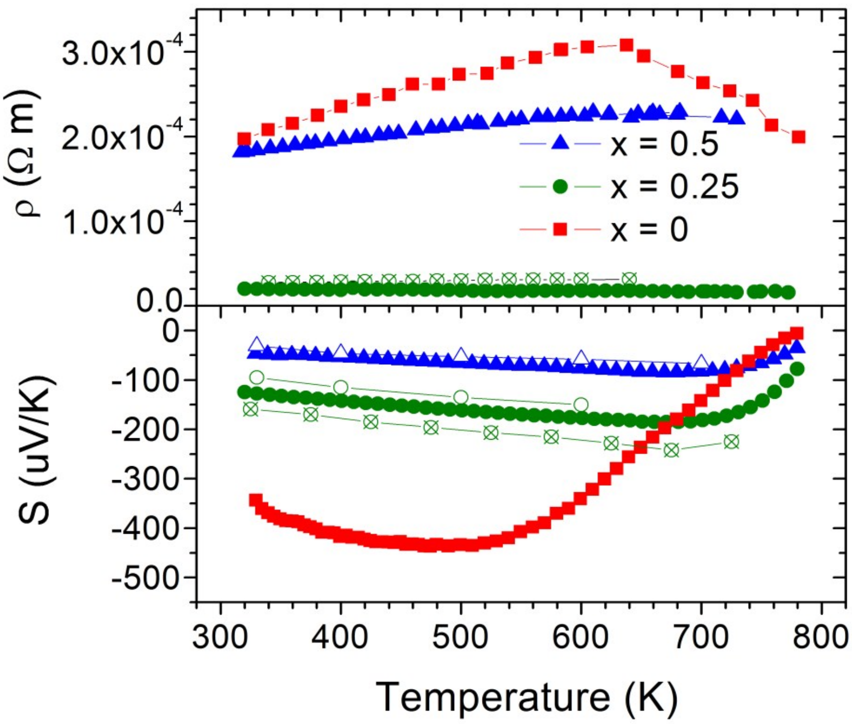


Figure ESI.3. Temperature dependence of electrical resistivity (top panel) and Seebeck coefficient (bot panel) of $La_xCo_4Sb_{12}$, x = 0 (red), 0.25 (green), 0.5 (blue). The reproducibility has been checked in several samples (open symbols).



Due to the extreme conditions of synthesis, the structure does not admit all the La that is loaded as precursors. However, this La is still present within the resulting pellet, in the form of various sorts of presumably insulating impurities between grains of the proper filled skutterudite. Thus, in this high-pressure synthesis, extra nominal La actually makes the resistivity worse (higher), and this effect is more conspicuous in the nominal $La_{0.5}Co_4O_{12}$ sample, yet additionally contributes to decrease the thermal conductivity. As Figure ESI.3 crucially demonstrates, the low resistivity (as well as other properties) of nominally $La_{0.25}Co_4Sb_{12}$ is very well reproducible.

Figure ESI.4. Temperature dependence of thermal conductivity of $La_xCo_4Sb_{12}$ (x = 0, 0.25, 0.5).