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The Impact of Site Selectivity and Disorder on the Thermoelectric Properties of $Yb_{21}Mn_4Sb_{18}$ solid solutions: $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ and $Yb_{21-y}Ca_yMn_4Sb_{18}$

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SUPPORTING INFORMATION

Table S1: Rietveld Refinement Results for $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ with $2\theta = 2° - 35°$ from Synchrotron Powder X-ray Diffraction (11-BM)

Composition	*x* = 0.5	*x* = 1.0	*x* = 1.5
Wavelength	0.457844 Å		
Crystal System	Monoclinic		
Space Group	C2/c		
Unit Cell Dimensions	a = 17.0365(2) Å b = 17.0266(2) Å c = 16.7977(2) Å β = 92.7775(5)°	a = 17.0176(4) Å b = 17.0267(4) Å c = 16.8062(3) Å β = 92.718(1)°	a = 17.0449(2) Å b = 17.0000(2) Å c = 16.8422(2) Å β = 92.7222(6)°
Volume (Å^3)	4866.8(1)	4864.2(2)	4874.7(1)
Cd Site Occupation (free)	Mn1 = 0.29(4) Mn2 = 0.00(3) Mn3 = 0.05(3) Mn4 = 0.22(3) Total Cd = 0.57(7) R_{wp} = 6.906	Mn1 = 0.75(7) Mn2 = 0.00(8) Mn3 = 0.18(5) Mn4 = 0.11(7) Total Cd = 1.0(1) R_{wp} = 8.552	Mn1 = 0.88(3) Mn2 = 0.00(3) Mn3 = 0.07(3) Mn4 = 0.31(3) Total Cd = 1.3(1) R_{wp} = 5.831
Refined Composition (free)	$Yb_{21}Mn_{3.43(7)}Cd_{0.57(7)}Sb_{18}$	$Yb_{21}Mn_{3.0(1)}Cd_{1.0(1)}Sb_{18}$	$Yb_{21}Mn_{2.7(1)}Cd_{1.3(1)}Sb_{18}$
Cd Site Occupation (constrained occ.)	Mn1 = 0.25(5) Mn2 = 0.00(3) Mn3 = 0.00(3) Mn4 = 0.25(3) Total Cd = 0.500 R_{wp} = 6.907	Mn1 = 0.65(11) Mn2 = 0.00(3) Mn3 = 0.35(5) Mn4 = 0.00(6) Total Mn = 1.000 R_{wp} = 8.532	Mn1 = 0.96(5) Mn2 = 0.00(3) Mn3 = 0.20(3) Mn4 = 0.34(2) Total Mn = 1.500 R_{wp} = 5.834
Mn1 – Mn2	3.64(3) Å	3.74(5) Å	4.004(2) Å
Mn2 – Mn3	2.35(3) Å	2.40(5) Å	2.07(3) Å
Mn3 – Mn4	2.75(2) Å	2.63(3) Å	2.65(3) Å

Table S2: Rietveld Refinement Results for $Yb_{21-y}Ca_yMn_4Sb_{18}$ with $2\theta = 2° - 35°$ from Synchrotron Powder X-ray Diffraction (11-BM)

Composition	y = 3.0	y = 6.0	y = 9.0	y = 10.5
Wavelength	0.457844 Å			
Crystal System	Monoclinic			
Space Group	*C*2/*c*			
Unit Cell Dimensions	a = 17.0580(2) Å b = 17.0566(2) Å c = 16.7969(2) Å β = 92.8587(4)°	a = 17.0845(2) Å b = 17.0649(2) Å c = 16.8196(2) Å β = 92.9170(4)°	a = 17.1042(2) Å b = 17.0694(2) Å c = 16.8373(2) Å β = 92.9772(4)°	a = 17.1160(2) Å b = 17.0665(2) Å c = 16.8523(2) Å β = 93.0095(4)°
Volume (Å^3)	4880.99(8)	4897.32(8)	4909.2(1)	4915.96(9)
Ca Site Occupation (free)	Yb1: 0.202(6) Yb2: 0.204(7) Yb3: 0.126(6) Yb4: 0.224(7) Yb5: 0.140(7) Yb6: 0.096(7) Yb7: 0.157(7) Yb8: 0.173(7) Yb9: 0.159(8) Yb10: 0.137(7) Yb11: 0.242(9) Total Ca: 1.86(2) R_{wp}: 6.945	Yb1: 0.290(6) Yb2: 0.370(7) Yb3: 0.237(6) Yb4: 0.357(7) Yb5: 0.267(8) Yb6: 0.218(7) Yb7: 0.297(8) Yb8: 0.327(8) Yb9: 0.343(8) Yb10: 0.281(7) Yb11: 0.392(9) Total Ca: 3.38(2) R_{wp}: 6.187	Yb1: 0.427(6) Yb2: 0.519(7) Yb3: 0.345(6) Yb4: 0.502(7) Yb5: 0.447(8) Yb6: 0.386(6) Yb7: 0.467(7) Yb8: 0.508(8) Yb9: 0.501(8) Yb10: 0.462(7) Yb11: 0.479(9) Total Ca: 5.04(2) R_{wp}: 6.374	Yb1: 0.498(5) Yb2: 0.581(5) Yb3: 0.421(5) Yb4: 0.554(5) Yb5: 0.542(6) Yb6: 0.475(5) Yb7: 0.532(6) Yb8: 0.584(6) Yb9: 0.542(6) Yb10: 0.553(5) Yb11: 0.552(7) Total Ca: 5.83(2) R_{wp}: 5.834
Refined Composition (free)	$Yb_{17.45(2)}Ca_{3.55(2)}Mn_4Sb_{18}$	$Yb_{14.55(2)}Ca_{6.45(2)}Mn_4Sb_{18}$	$Yb_{11.38(2)}Ca_{9.62(2)}Mn_4Sb_{18}$	$Yb_{9.86(2)}Ca_{11.13(2)}Mn_4Sb_{18}$
Ca Site Occupation (constrained Occ)	Yb1: 0.167(6) Yb2: 0.188(7) Yb3: 0.103(6) Yb4: 0.198(7) Yb5: 0.133(8) Yb6: 0.068(7) Yb7: 0.110(8) Yb8: 0.157(8) Yb9: 0.121(8) Yb10: 0.115(7) Yb11: 0.212(8) Total Ca: 1.57143 R_{wp}: 6.853	Yb1: 0.276(6) Yb2: 0.358(7) Yb3: 0.215(6) Yb4: 0.337(7) Yb5: 0.240(8) Yb6: 0.199(7) Yb7: 0.291(8) Yb8: 0.299(8) Yb9: 0.324(8) Yb10: 0.256(7) Yb11: 0.349(9) Total Ca: 3.14286 R_{wp}: 6.177	Yb1: 0.395(6) Yb2: 0.496(7) Yb3: 0.327(6) Yb4: 0.470(6) Yb5: 0.425(8) Yb6: 0.358(6) Yb7: 0.443(8) Yb8: 0.486(8) Yb9: 0.465(8) Yb10: 0.434(7) Yb11: 0.415(8) Total Ca: 4.71429 R_{wp}: 6.385	Yb1: 0.467(5) Yb2: 0.559(5) Yb3: 0.400(5) Yb4: 0.522(5) Yb5: 0.524(6) Yb6: 0.448(5) Yb7: 0.506(6) Yb8: 0.563(6) Yb9: 0.503(7) Yb10: 0.528(5) Yb11: 0.480(7) Total Ca: 5.5 R_{wp}: 5.409

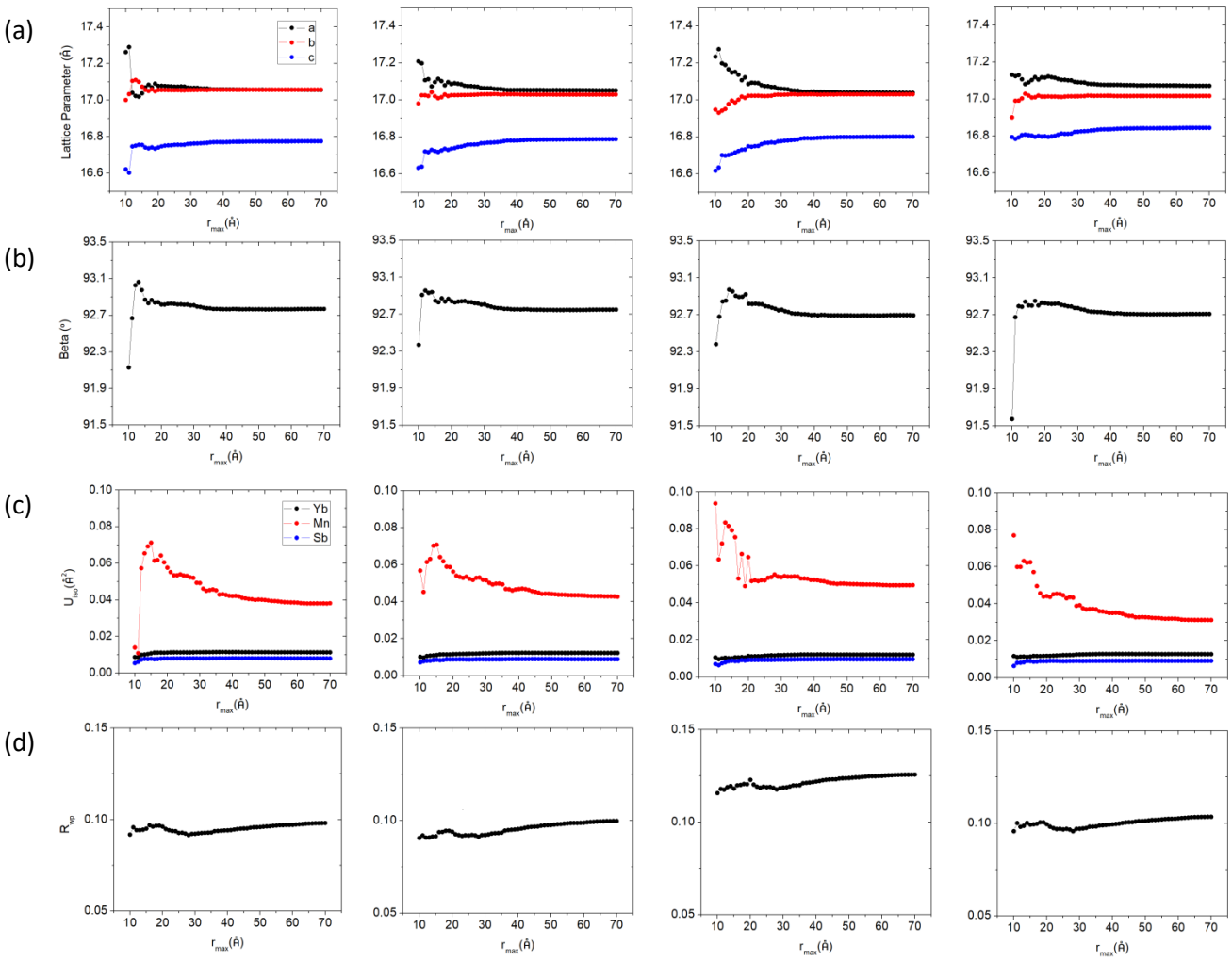

Figure S1: Total X-ray Scattering refinement results for $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ (x = 0, 0.5, 1.0, 1.5) showing (a) Lattice parameters, (b) beta angle, (c) atomic displacement parameters, (d) R_{wp} value.

Table S3: Total X-ray Scattering Refinement Results for $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ (x = 0, 0.5, 1.0, 1.5) with a Restricted r_{max} = 70 Å

Composition	x = 0	x = 0.5	x = 1.0	x = 1.5
Wavelength	0.2115 Å			
Crystal System	Monoclinic			
Space Group	C2/c			
Unit Cell Dimensions	a = 17.0558Å b = 17.057Å c = 16.775Å β = 92.7695°	a = 17.0514 Å b = 17.0291 Å c = 16.7873 Å β = 92.7507°	a = 17.0386 Å b = 17.0305 Å c = 16.7998 Å β = 92.6999°	a = 17.0715 Å b = 17.0163 Å c = 16.8441Å β = 92.7107°
U_{iso}	Yb = 0.011356 Å^2 Mn = 0.038174 Å^2 Sb = 0.008016 Å^2	Yb = 0.012259 Å^2 Mn = 0.04267Å^2 Sb = 0.0089 Å^2	Yb = 0.011992 Å^2 Mn = 0.05343Å^2 Sb = 0.009549 Å^2	Yb = 0.012778Å^2 Mn = 0.031206 Å^2 Sb = 0.009141 Å^2
R_{wp}	0.09816	0.099837	0.125745	0.103506

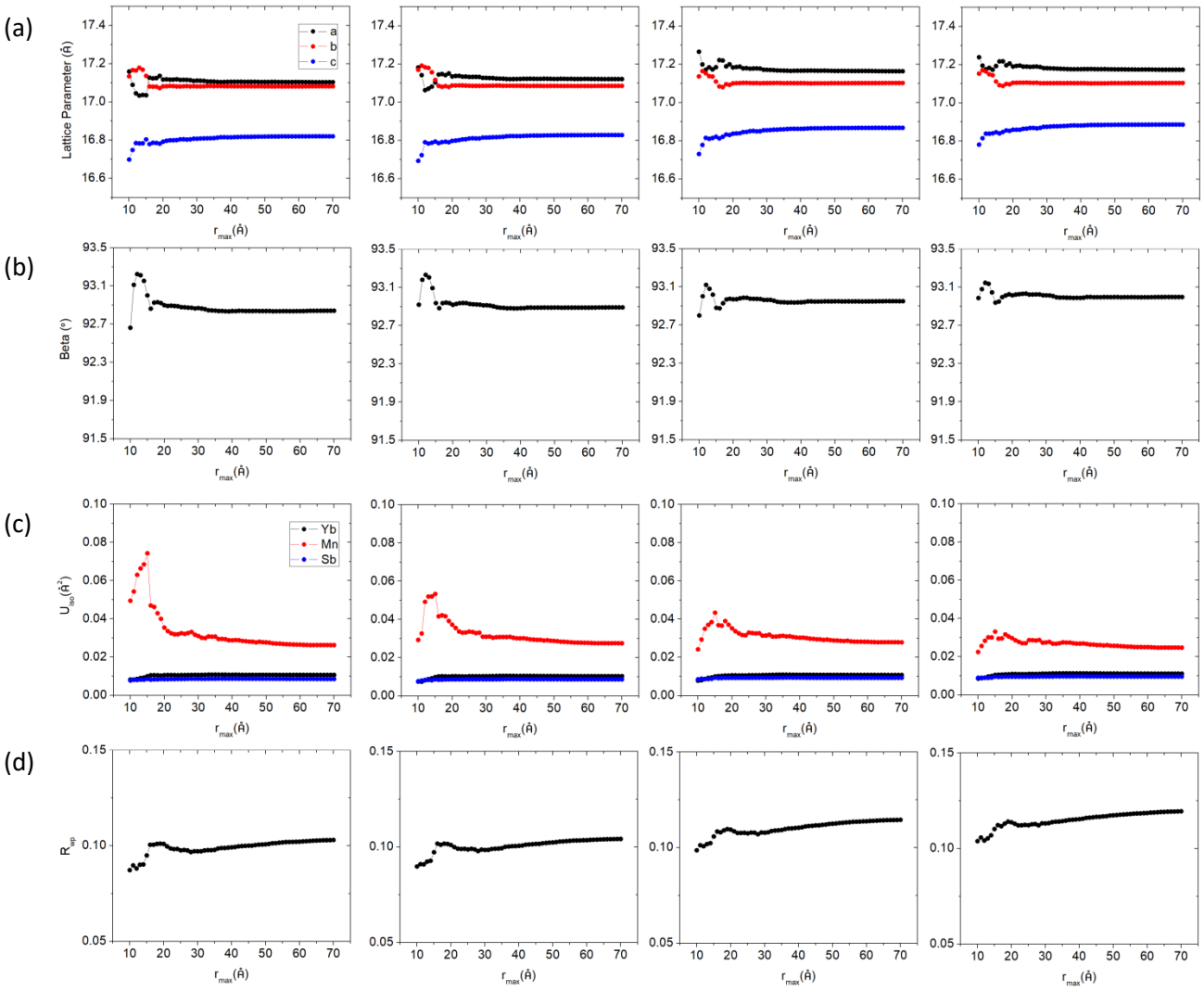

Figure S2: Total X-ray Scattering refinement results for $Yb_{21-y}Ca_yMn_4Sb_{18}$ (y = 3, 6, 9, 10.5) showing (a) Lattice parameters, (b) beta angle, (c) atomic displacement parameters, (d) R_{wp} value.

Table S4: Total X-ray Scattering Refinement Results for $Yb_{21-y}Ca_yMn_4Sb_{18}$ (y = 3, 6, 9, 10.5) with a Restricted r_{max} = 70 Å

Composition	y = 3.0	y = 6.0	y = 9.0	y = 10.5
Wavelength	0.2115 Å			
Crystal System	Monoclinic			
Space Group	C2/c			
Unit Cell Dimensions	a = 17.1034 Å b = 17.0821 Å c = 16.8201 Å β = 92.8404°	a = 17.1214Å b = 17.0857Å c = 16.8284Å β = 92.8918°	a = 17.1643Å b = 17.1026 Å c = 16.8679 Å β = 92.95°	a = 17.1736 Å b = 17.1044 Å c = 16.8864 Å β = 92.9974°
U_{iso}	Yb = 0.01063 Å^2 Mn = 0.026261 Å^2 Sb = 0.008568 Å^2	Yb = 0.010348 Å^2 Mn = 0.027556 Å^2 Sb = 0.008664 Å^2	Yb = 0.010761 Å^2 Mn = 0.027916 Å^2 Sb = 0.009294 Å^2	Yb = 0.011148 Å^2 Mn = 0.024777 Å^2 Sb = 0.009637 Å^2
R_{wp}	0.103003	0.104197	0.114528	0.119490

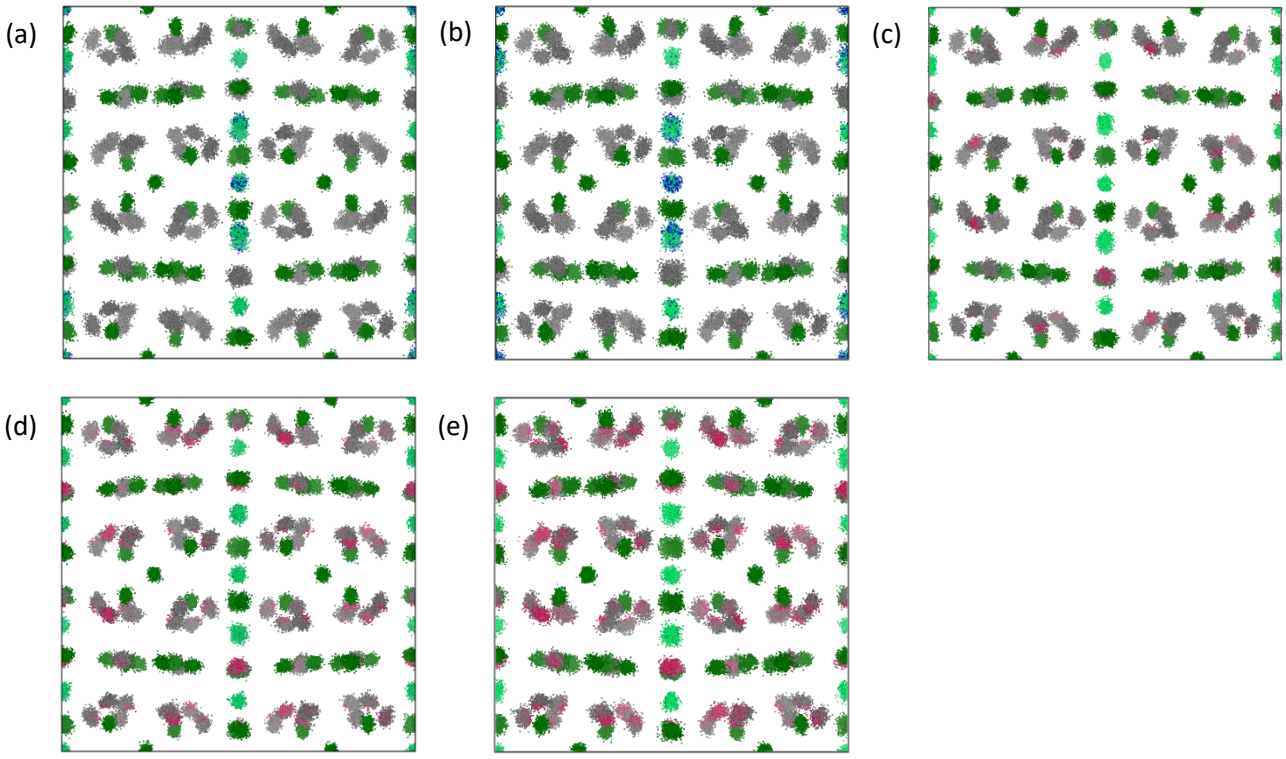

Figure S3. Point-cloud distributions for $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ and $Yb_{21-y}Ca_yMn_4Sb_{18}$ a) x = 0.5, b) x = 1.0, c) y = 3, d) y = 6, e) y = 9.

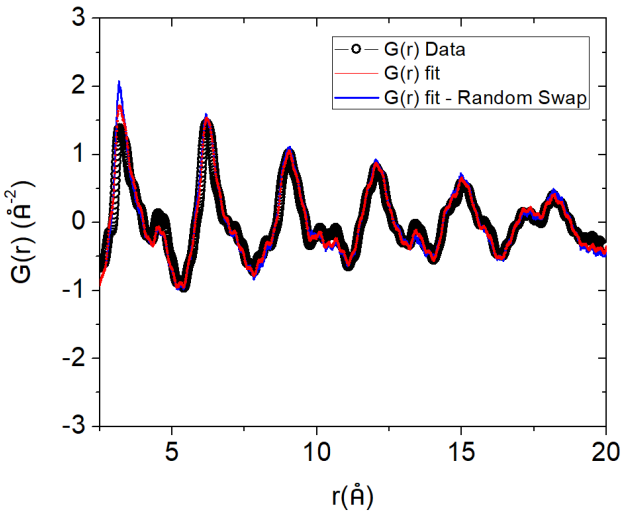

Figure S4. Reverse Monte Carlo fit for sample $Yb_{10.5}Ca_{10.5}Mn_4Sb_{18}$ before (red) and after (blue) 12h random swapping of Ca and Yb atoms.

Table S5: Experimental Energy Dispersive X-ray Spectroscopy Results for $Yb_{21}Mn_{4-x}Cd_xSb_{18}$ (x = 0.5, 1.0, 1.5) Pellets

$Yb_{21}Mn_{4-x}Cd_xSb_{18}$	Yb (at. %)	Mn (at. %)	Cd (at. %)	Sb (at. %)
$Yb_{21}Mn_{3.5}Cd_{0.5}Sb_{18}$ (nominal) (x = 0.5)	48.84	8.14	1.16	41.86
$Yb_{21}Mn_{3.5}Cd_{0.5}Sb_{18}$ (EDS) (x = 0.5)	48(3)	8.1(4)	1.4(1)	43(2)
$Yb_{21}Mn_{3.0}Cd_{1.0}Sb_{18}$ (nominal) (x = 1.0)	48.84	6.98	2.32	41.86
$Yb_{21}Mn_{3.0}Cd_{1.0}Sb_{18}$ (EDS) (x = 1.0)	48(2)	6.9(3)	2.6(1)	43(2)
$Yb_{21}Mn_{2.5}Cd_{1.5}Sb_{18}$ (nominal) (x = 1.5)	48.84	5.81	3.49	41.86
$Yb_{21}Mn_{2.5}Cd_{1.5}Sb_{18}$ (EDS) (x = 1.5)	48(2)	6.0(2)	3.7(1)	43(1)

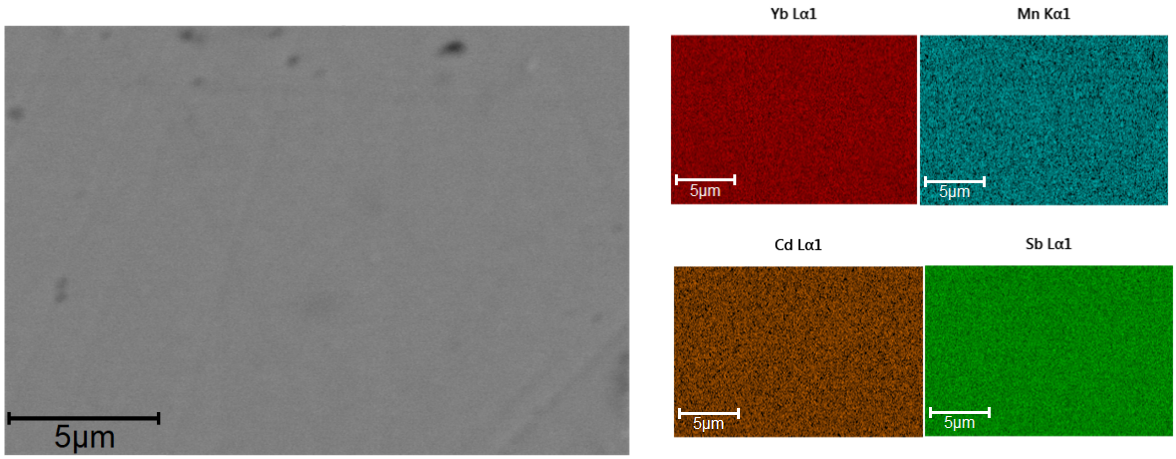

Figure S5. Backscattered electron images of x = 1.0 sample ($Yb_{21}Mn_3CdSb_{18}$) (left) after SPS along with elemental mapping (right).

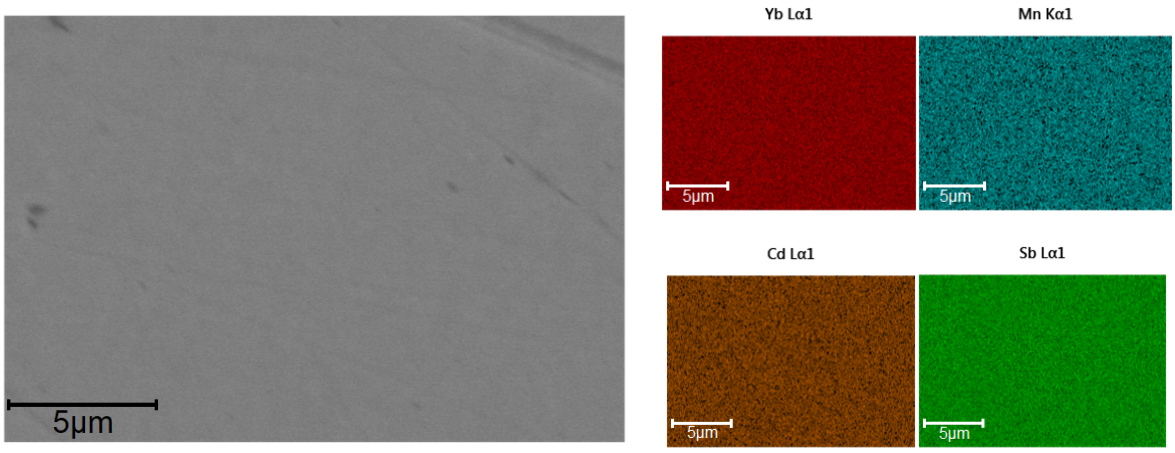

Figure S6. Backscattered electron images of x = 1.5 sample ($Yb_{21}Mn_{2.5}Cd_{1.5}Sb_{18}$) (left) after SPS along with elemental mapping (right).

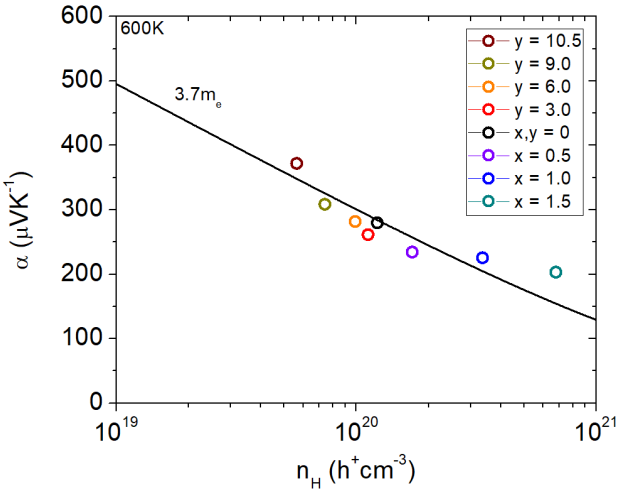

Figure S7. Pisarenko plot for the Cd-substituted ($Yb_{21}Mn_{4-x}Cd_xSb_{18}$) samples and Ca-substituted ($Yb_{21-y}Ca_yMn_4Sb_{18}$) samples.

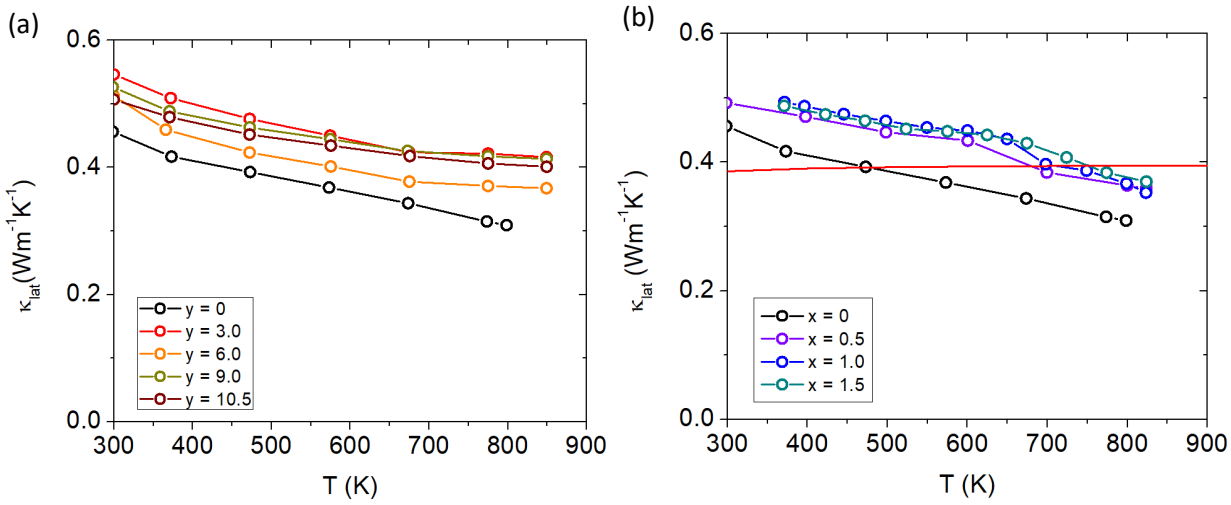

Figure S8. Lattice Thermal Conductivities for the a) Ca-substituted samples and b) Cd-substituted samples, plotted with κ_{min} of the parent (*x* = 0) sample (red line) determined from speed of sound measurements.