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Materials design, synthesis, and transport properties of disordered rare-earth Zintl bismuthides with the *anti*-Th_3P_4 structure type

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Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Ce1[a]	16*c*	0.07103(5)	*x*	*x*	0.0113(4)
Sb1	12*a*	3/8	0	1/4	0.0100(2)

[a]Atomic occupancies according to refinement: Ca1/Ce1 = 0.822(7)Ca + 0.178Ce.

Table S2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.35(1)}Pr_{0.66}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Pr1[a]	16*c*	0.0721(1)	*x*	*x*	0.0067(9)
Bi1	12*a*	3/8	0	1/4	0.0068(3)

[a]Atomic occupancies according to refinement: Ca1/Pr1 = 0.836(8)Ca + 0.164Pr.

Table S3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.33(1)}Nd_{0.67}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Nd1[a]	16*c*	0.0719(2)	*x*	*x*	0.0084(8)
Bi1	12*a*	3/8	0	1/4	0.0084(2)

[a]Atomic occupancies according to refinement: Ca1/Nd1 = 0.833(6)Ca + 0.167Nd.

Table S4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.23(1)}Sm_{0.77}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Sm1[a]	16*c*	0.0719(1)	*x*	*x*	0.0087(7)
Bi1	12*a*	3/8	0	1/4	0.0083(2)

[a]Atomic occupancies according to refinement: Ca1/Sm1 = 0.807(6)Ca + 0.193Sm.

Table S5. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.23(1)}Gd_{0.77}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Gd1[a]	16*c*	0.0723(1)	*x*	*x*	0.0073(7)
Bi1	12*a*	3/8	0	1/4	0.0065(2)

[a]Atomic occupancies according to refinement: Ca1/Gd1 = 0.808(7)Ca + 0.192Gd.

Table S6. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.35(1)}Tb_{0.65}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Tb1[a]	16*c*	0.0725(1)	*x*	*x*	0.011(1)
Bi1	12*a*	3/8	0	1/4	0.010(1)

[a]Atomic occupancies according to refinement: Ca1/Tb1 = 0.837(10)Ca + 0.163Tb.

Table S7. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.33(1)}Dy_{0.67}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Dy1[a]	16*c*	0.0724(1)	*x*	*x*	0.0090(7)
Bi1	12*a*	3/8	0	1/4	0.0096(2)

[a]Atomic occupancies according to refinement: Ca1/Dy1 = 0.833(4)Ca + 0.167Dy

Table S8. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.38(1)}Ho_{0.62}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Ho1[a]	16*c*	0.07252(9)	*x*	*x*	0.0095(6)
Bi1	12*a*	3/8	0	1/4	0.0097(2)

[a]Atomic occupancies according to refinement: Ca1/Ho1 = 0.844(5)Ca + 0.156Ho.

Table S9. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.27(1)}Er_{0.73}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Er1[a]	16*c*	0.0727(2)	*x*	*x*	0.011(1)
Bi1	12*a*	3/8	0	1/4	0.010(1)

[a]Atomic occupancies according to refinement: Ca1/Er1 = 0.818(8)Ca + 0.182Er.

Table S10. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Ca_{3.25(1)}Tm_{0.75}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Tm1[a]	16*c*	0.0725(1)	*x*	*x*	0.0091(9)
Bi1	12*a*	3/8	0	1/4	0.0106(3)

[a]Atomic occupancies according to refinement: Ca1/Tm1 = 0.813(7)Ca + 0.187Tm.

Table S11. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.47(1)}Lu_{0.5}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Lu1[a]	16*c*	0.07235(9)	*x*	*x*	0.0116(5)
Bi1	12*a*	3/8	0	1/4	0.0151(3)

[a]Atomic occupancies according to refinement: Ca1/Lu1 = 0.865(6)Ca + 0.135Lu.

Table S12. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.29(1)}Y_{0.71}Bi_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Y1[a]	16*c*	0.0728(2)	*x*	*x*	0.011(1)
Bi1	12*a*	3/8	0	1/4	0.0096(2)

[a]Atomic occupancies according to refinement: Ca1/Y1 = 0.823(18)Ca + 0.177Y.

Table S13. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for $Ca_{3.2}Ho_{0.8}Bi_{1.67(1)}Sb_{1.33}$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	**Site**	***x***	***y***	***z***	U_{eq}
Ca1/Ho1[a]	16*c*	0.07250(2)	*x*	*x*	0.009(1)
Bi1/Sb1[b]	12*a*	3/8	0	1/4	0.009(1)

[a]Atomic occupancies of Ca and Ho were fixed according to the ratio Ca/Ho = 0.8Ca + 0.2Ho.
[b]Atomic occupancies according to refinement: Bi1/Sb1 = 0.56(4)Bi + 0.44(4)Sb.

Table S14. Selected crystallographic data of $Ca_3HoBi_{1.5}Sb_{1.5}$, measured at 200(2) K, space group $I\bar{4}3d$, $Z = 4$, Mo Kα radiation λ = 0.71073 Å.

refined formula	$Ca_{3.2}Ho_{0.8}Bi_{1.67(1)}Sb_{1.33}$
formula wt.	771.12
a/Å	9.4530(17)
V/Å^3	844.7(4)
ρ_{cal}/g cm^{-3}	6.06
μ/cm^{-1}	481.5
R_1 ($I \geq 2\sigma_I$)[a]	0.0376
wR_2 ($I \geq 2\sigma_I$)[a]	0.0768
R_1 (all data)[a]	0.0403
wR_2 (all data)[a]	0.0775
largest diff. peak and hole	2.69; –1.25

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2F_o^2+(0.0236P)^2+(83.284P)]$, and $P = (F_o^2+2F_c^2)/3$.

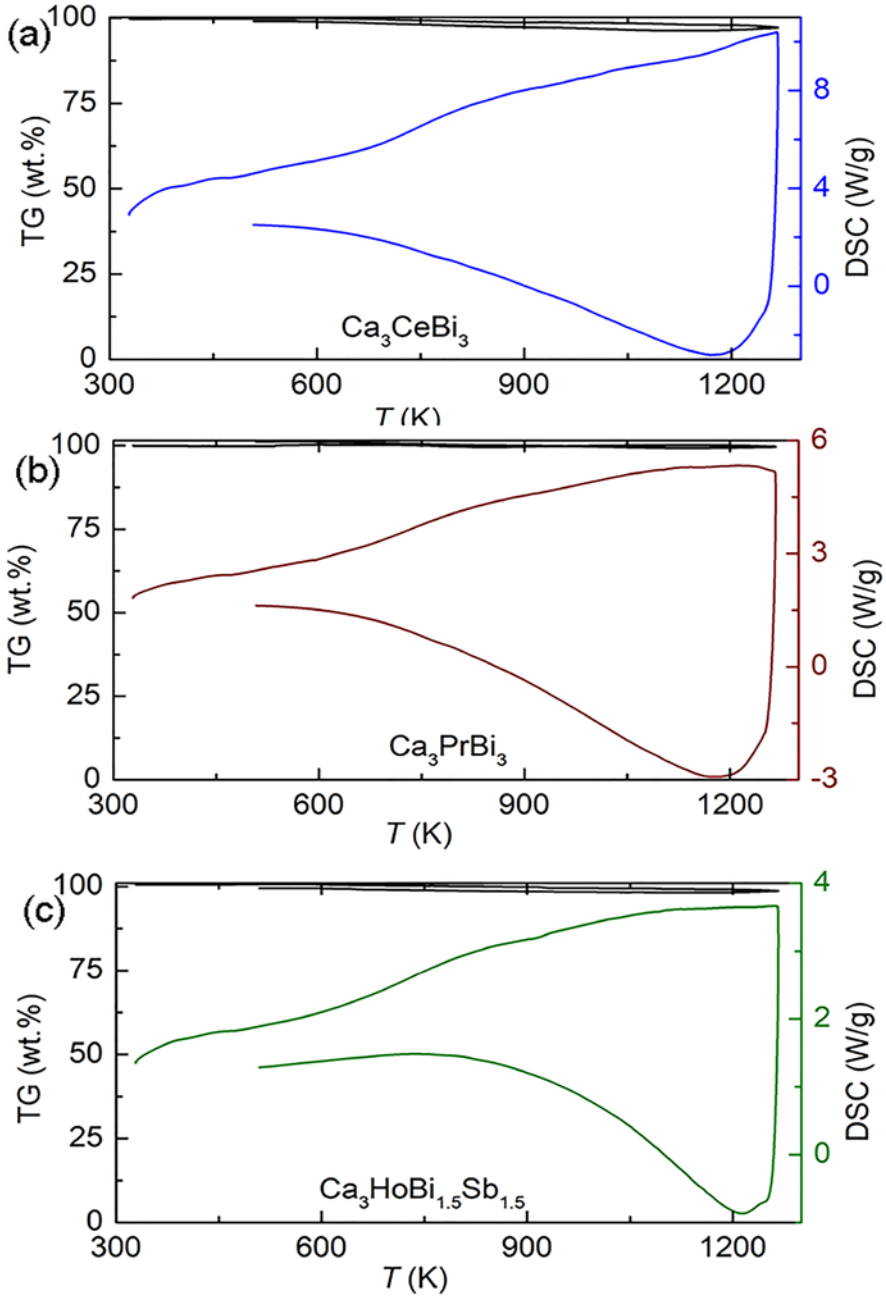

Figure S1. Plots of TG/DSC analysis for (a) Ca_3LaBi_3 (b) Ca_3PrBi_3 and (c) $Ca_3HoBi_{1.5}Sb_{1.5}$ samples. The weight (wt.) % and heat flows are represented as blue, brown, and green lines, respectively.

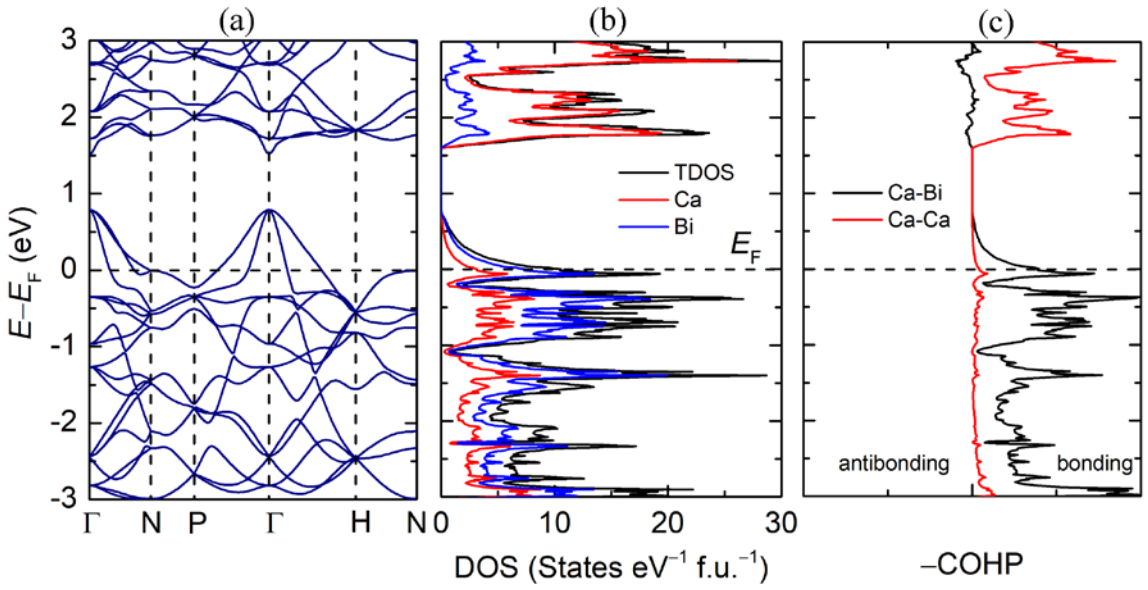

Figure S2. (a) Electronic band structure of Ca_4Bi_3. (b) Total density of states (TDOS) and orbital resolved DOS of Ca_4Bi_3. (c) calculated COHP curves for Ca–Bi and Ca–Ca interactions for Ca_4Bi_3. COHP are showing the bonding and antibonding states as indicated. The Fermi energy is set as a reference point at 0 eV.

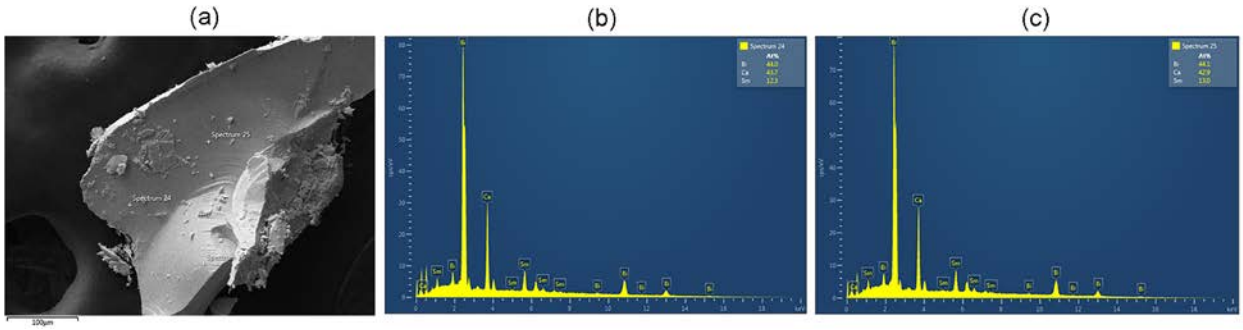

Figure S3. (a) SEM image of single crystal of Ca_3SmBi_3. (b) and (c) Representative histograms from EDS analysis of Ca_3SmBi_3 under high magnification.

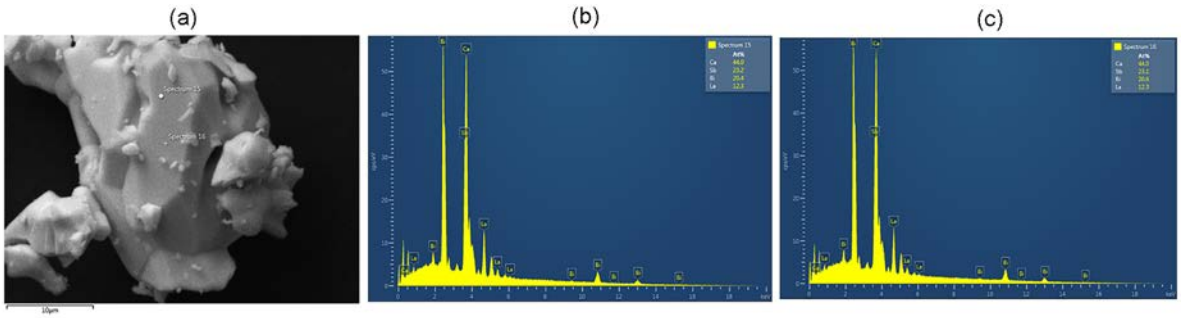

Figure S4. (a) SEM image of single crystal of $Ca_3LaBi_{1.5}Sb_{1.5}$. (b) and (c) Representative histograms from EDS analysis of Ca_3SmBi_3 under high magnification.