Electronic Supplementary Information (ESI)

Lone-pair stabilized channels in apatite-related structures

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Table S1. Crystal data and structure refinement for $Tb_2Pb_3Si_3O_{12}$ at 293(2) K.

Empirical formula	$Tb_2Pb_3Si_3O_{12}$
Formula weight	1215.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	hexagonal
Space group	$P6_3/m$
Unit cell dimensions	a = 9.6395(2) Å c = 6.8787(2) Å
Volume	553.54(3) $Å^3$
Z	2
Density (calculated)	7.294 g/cm^3
θ range for data collection	2.440 to 29.068°
Index ranges	-12<=h<=13, -12<=k<=12, -6<=l<=9
Reflections collected	5914
Independent reflections	522 [R_{int} = 0.0667]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	522 / 0 / 37
Goodness-of-fit	1.136
Final R indices [I > 2σ(I)]	R_{obs} = 0.0442, wR_{obs} = 0.1208
R indices [all data]	R_{all} = 0.0460, wR_{all} = 0.1221

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0653P)^2+27.4284P]$ where $P=(Fo^2+2Fc^2)/3$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $Tb_2Pb_3Si_3O_{12}$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Pb	-0.0057(1)	0.7538(7)	0.7500	1	0.021(1)
Tb	0.3333(4)	0.6667(12)	0.5038(4)	1	0.010(1)
Si	0.4139(6)	1.0302(6)	0.7500	1	0.010(1)
O(1)	0.3533(18)	0.8400(16)	0.7500	1	0.017(3)
O(2)	0.6080(15)	1.1385(15)	0.7500	1	0.019(3)
O(3)	0.3635(17)	1.0953(14)	0.9420(14)	1	0.035(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Bond lengths [Å] for $Tb_2Pb_3Si_3O_{12}$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Pb-O(1)	2.375(13)
Pb-O(2)x2	2.384(12)
Pb-O(2)'x2	2.562(14)
Tb-O(1)x3	2.319(9)
Tb-O(2)x3	2.415(7)
Tb-O(3)x3	2.698(14)
Si-O(1)	1.622(13)
Si-O(2)	1.624(5)
Si-O(3)	1.638(14)
Si-O(4)	1.638(12)

Table S4. Selected Bond angles [°] for $Tb_2Pb_3Si_3O_{12}$ at 293(2) K

Label	Angles
O(1)-Pb-O(2)	84.6(3)
O(1)-Pb-O(2)'	69.5(4)
O(2)'-Pb-O(2)	62.0(7)
O(3)-Tb-O(3)	72.7(4)
O(3)-Tb-O(1)	93.5(3)
O(3)-Tb-O(1)	146.8(4)
O(3)-Tb-O(2)	142.0(5)
O(3)-Tb-O(2)'	80.6(4)
O(3)-Si-O(1)	111.8(7)

O(3)-Si-O(2)	115.0(5)

Table S5. Crystal data for $Pb_5SiP_2O_{12}$ at 293(2) K.

Empirical formula	$Pb_5SiP_2O_{12}$
Formula weight	2636.07
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	hexagonal
Space group	$P6_3/m$
Unit cell dimensions	a = 9.7637(14) Å c = 7.2791(15) Å
Volume	600.9(2) $Å^3$
Z	2
Density (calculated)	7.284 g/cm^3
θ range for data collection	2.409 to 27.430°
Index ranges	-12<=h<=10, -12<=k<=12, -9<=l<=9
Reflections collected	5643
Independent reflections	495 [R_{int} = 0.0991]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	495 / 0 / 24
Goodness-of-fit	1.437
Final R indices [I > 2σ(I)]	R_{obs} = 0.0571, wR_{obs} = 0.1043
R indices [all data]	R_{all} = 0.0590, wR_{all} = 0.1051
Extinction coefficient	0.0054(5)

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+57.6948P]$ where $P=(Fo^2+2Fc^2)/3$

Table S6. Atomic coordinates and equivalent isotropic displacement parameters for $Pb_5SiP_2O_{12}$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Pb(1)	0.2503(12)	0.0002(2)	0.2500	1	0.014(1)
Pb(2)	0.3333.33	-0.3333.33	0.0042(4)	1	0.013(3)
Si(3)	0.6210(7)	0.0187(8)	0.2500	0.333	0.003(2)
P(3)	0.6210(7)	0.0187(8)	0.2500	0.6666	0.003(2)

O(1)	0.5060(12)	0.0930(12)	0.2500	1	0.012(4)
O(2)	0.7292(17)	0.0786(17)	0.4218(17)	1	0.012(3)
O(3)	0.5200(13)	-0.1660(14)	0.2500	1	0.010(6)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Selected bond lengths [Å] for $Pb_5SiP_2O_{12}$ at 293(2) K.

Label	Distances
Pb(1)-O(1)	2.19(2)
Pb(1)-O(2)'x2	2.631(11)
Pb(1)-O(2)x2	2.548(14)
Pb(1)-O(3)	2.75(2)
Pb(2)-O(2)x3	2.75(2)
Pb(2)-O(3)x3	2.492(8)
Si/P(3)-O(1)	1.61(4)
Si/P(3)-O(2)x2	1.550(13)
Si/P(3)-O(3)	1.56(2)

Table S8. Selected bond angles [°] for $Pb_5SiP_2O_{12}$ at 293(2) K.

Label	Angles
O(1)-Pb(1)-O(1)'	139.0(6)
O(1)-Pb(1)-O(3)	150.8(7)
O(1)-Pb(1)-O(3)'	71.7(3)
O(1)-Pb(1)-O(2)	79.3(6)
O(2)-Pb(1)-O(3)	95.7(7)
O(1)-(P/Si)-O(1)'	108.1(11)
O(1)-(P/Si)-O(2)	108.8(8)
O(1)-(P/Si)-O(3)	110.7(7)

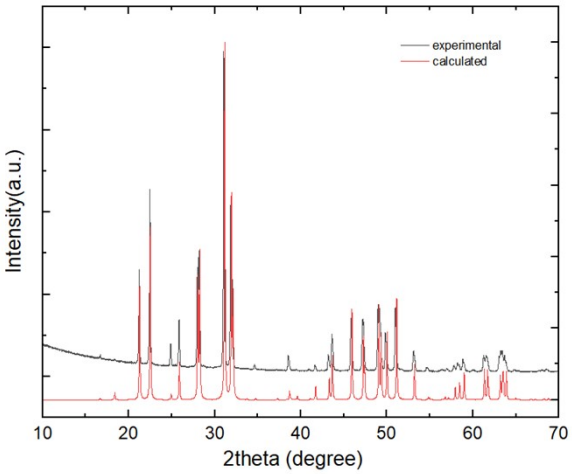

Figure S1. PXRD patterns for $Tb_2Pb_3Si_3O_{12}$