Table S1. Crystal data and structure refinement for new K,Sc-phosphates.

formula	**$KSc(HPO_4)_2$ (I)**	**$KSc(HPO_4)_2$ (I')**	**$K_3Sc_3(P_3O_{10}F_2)F_5$ (III)**
formula weight (g/mol)	276.01	276.01	638.09
T (K)	293	150	150
crystal system	Orthorhombic	Monoclinic	Orthorhombic
space group, Z	*Pnam*, 4	$P\,1\,2_1/c\,1$, 4	$Cmc2_1$, 4
Unit cell parameters	*a* =14.5271(6) Å	*a* = 5.4366(3) Å	*a* =15.6067(9) Å
	b =8.4948(3)Å	*b* = 8.4565(4) Å	*b* =8.8198(5) Å
	c = 5.4375(2)Å	*c* = 14.4529(8) Å	*c* =11.2063(6) Å
		β = 90.185(4) º	
V (Å ^{3})	671.01(4)	664.46(6)	1542.52(15)
crystal size (mm)	0.15x0.03x0.03	0.15x0.03x0.03	0.1x0.04x0.01
ρ_{calcd} (g/cm ^{3})	2.712	2.739	2.748
μ (mm^{-1})	2.200	2.221	2.527
F(000)	536	536	1232
wavelength (Å)	0.71073	0.71073	0.71073
θ range/deg.	2.778 - 27.868	2.791 - 27.873	2.653 - 28.277
limiting indices	$-18 \le h \le 19$,	$-7 \le h \le 7$,	$-20 \le h \le 20$,
	$-11 \le k \le 11$,	$-11 \le k \le 11$,	$-11 \le k \le 11$,
	$-7 \le l \le 7$	$-18 \le l \le 18$	$-14 \le l \le 14$
refl. collected / unique	4577 / 882	6175 / 1570	6613 / 1966
Rint	0.0263	0.0326	0.0536
completeness to theta,%	100	100	99.9
data / restraints / parameters	882 / 0 / 67	1570 / 0 / 99	1966 / 1 / 117
GOF	1.108	1.151	1.152
R_1, wR_2 [a] [$I > 2\sigma(I)$]	0.0330, 0.0947	0.0653, 0.1797	0.0535, 0.1174
R_1, wR_2 (all data) [a]	0.0357, 0.0974	0.0682, 0.1813	0.0643, 0.1385
Δρ max and Δρ min (e.Å $^{-3}$)	1.001 and -0.731	1.087 and -1.390	1.442 and -1.534

[a] $R(F) = \sum || F_o | - | F_c || / \sum | F_o |$ and $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $KSc(HPO_4)_2$ (I) and $KSc(HPO_4)_2$ (I'). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	X	Y	Z	U_{eq}
		$KSc(HPO_4)_2$ (I)		
Sc	3766(1)	1697(1)	2500	5.6(2)
K	1202(1)	0335(1)	2500	25.7(3)
P1	5160(1)	2060(1)	7500	5.8(2)
P2	2178(1)	4776(1)	2500	6.3(2)
O1(OH)	6106(2)	3002(4)	7500	16.8(6)
O2	4658(1)	2614(2)	9799(4)	11.5(4)
O3	5364(2)	0312(3)	7500	11.6(5)
O4	3040(2)	3776(3)	2500	13.6(6)
O5	2105(1)	5762(2)	0179(4)	16.5(4)

O6(OH)	1345(2)	3559(4)	2500	17.2(6)
		$KSc(HPO_4)_2$ (I')		
Sc	7512(2)	8285(1)	6224(1)	2.5(3)
K	7329(4)	9663(2)	8795(1)	16.4(4)
P1	2519(3)	7941(2)	4833(1)	2.7(4)
P2	3176(12)	1588(6)	7191(11)	2.4(4)
O1	2499(9)	9709(6)	4658(3)	5.0(9)
O2	0243(9)	7368(6)	5345(3)	6.1(9)*
O3(OH)	2515(10)	7052(6)	3866(3)	9.2(10)
O4	5183(9)	4232(6)	7924(3)	8.6(10)*
O5	4838(9)	7362(6)	5315(3)	7.3(10)
O6	7459(9)	6186(6)	6947(3)	6.0(9)
O7	9818(9)	4187(6)	7871(4)	8.4(10)
O8(OH)	7651(11)	6427(6)	8644(4)	11.6(11)

* This atoms were refinement in isotropic approximation.

Table S3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $K_3Sc_3(P_3O_{10}F_2)F_5$ (III). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	X	Y	Z	U_{eq}
Sc1	5000	0691(3)	4749(3)	7.5(5)
Sc2	6256(1)	6916(2)	4661(2)	7.0(4)
K1	5000	5927(4)	1818(3)	15.2(7)
K2	7929(2)	4791(3)	2042(3)	20.3(6)
P1	6697(2)	3110(3)	4857(3)	9.4(6)
P2	5000	8134(5)	6854(4)	7.8(7)
F1	5000	6346(11)	4248(9)	12(2)
F2	6541(5)	6549(9)	2981(6)	15.2(15)
F3	5901(4)	9114(7)	4215(6)	11.2(13)
F4	6777(6)	6777(6)	3445(8)	28(2)
O1	4198(6)	7305(10)	6420(7)	11.6(17)
O2	5000	8097(13)	8209(10)	9(2)
O3	6503(6)	4723(10)	5194(7)	12.4(17)*
O4	5997(6)	2087(10)	5315(8)	12.5(17)
O5	5000	9774(15)	6420(11)	17(3)
O6	7565(6)	2657(9)	5313(7)	8.7(16)*

* This atoms were refinement in isotropic approximation.

Table S4. Selected interatomic distances for new K,Sc-phosphates.

Atoms	Bonds (Å)	Atoms	Bonds (Å)	Atoms	Bonds (Å)
(I)		**(I')**		**(III)**	
ScO_6 octahedron		ScO_6 octahedron		$Sc1O_4F_2$ octahedron	
Sc-O4	2.057(3)	Sc-O6	2.059(5)	Sc1-O2	2.030(12)
Sc-O5x2	2.087(2)	Sc-O4	2.078(5)	Sc1-O5	2.040(13)
Sc-O2x2	2.108(2)	Sc-O7	2.095(5)	Sc1-F3x2	2.066(7)

Sc-O3	2.123(3)	Sc-O2	2.105(5)	Sc1-O4x2	2.083(8)
$P1O_3(OH)$ tetrahedron		Sc-O5	2.106(5)	$Sc2O_3F_3$ octahedron	
P1-O3	1.514(3)	Sc-O1	2.122(5)	Sc2-F2	1.961(7)
P1-O2x2	1.522(2)	$P1O_3(OH)$ tetrahedron		Sc2-O3	2.060(9)
P1-O1(OH)	1.591(3)	P1-O1	1.517(5)	Sc2-F1	2.075(4)
$P2O_3(OH)$ tetrahedron		P1-O5	1.519(5)	Sc2-F3	2.077(7)
P2-O4	1.514(3)	P1-O2	1.522(5)	Sc2-O6	2.086(9)
P2-O5x2	1.519(2)	P1-O3(OH)	1.587(5)	Sc2-O1	2.123(8)
P2-O6(OH)	1.591(3)	$P2O_3(OH)$ tetrahedron		$P1O_3F$ tetrahedron	
		P2-O6	1.510(5)	P1-O6	1.501(9)
		P2-O4	1.516(5)	P1-O3	1.503(9)
		P2-O7	1.520(5)	P1-O4	1.507(9)
		P2-O8(OH)	1.583(5)	P1-F4	1.591(9)
				$P2O_4$ tetrahedron	
				P2-O2	1.519(11)
				P2-O5	1.526(14)
				P2-O1x2	1.528(9)