Table S1. Crystal data and structure refinement for $(Bi_{2,494}Na_{2,505})(PO_4)_3Cl$.

Formula	$(Bi_{2,494}Na_{2,505})(PO_4)_3Cl$
Formula weight	899.25
Crystal system	hexagonal
Space group, *Z*	*P*-6, 4
a, Å	9.7197(7)
c, Å	13.8019(10)
V, Å ^{3}	1129.2(1)
D_x, г/см ^{3}	5,29
μ, мм $^{-1}$	39.62
Wavelength, Å	0.71073
Θ range/degree	2.83- 30.77
Refl. collected/unique/$R_{int.}$	110703 / 2019/ 0.0546
Completeness to Θ, %	0.95
Parameters	140
GOF (S)	1.066
R_{all}, R_{gt}, R_{wgt}	0.0494, 0.0415, 0.0804
$\Delta\rho_{min}/\Delta\rho_{max}$, э/Å ^{3}	-1.652/ 2.144

[1] $R_{gt} = \Sigma. \, ||F_o| - |F_c|| = \Sigma |F_o|$ and $R_{wgt} = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ *for* $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates and equivalent displacement parameters for $(Bi_{2,494}Na_{2,505})(PO_4)_3Cl$.

Atom	Wyckoff notation, symmetry, multiplicity	Composition	*x/a*	*y/b*	*z/c*	U_{equ}, Å^2
M1(Bi2)*	3j, *m,* 0.5	Bi	0.2582(1)	0.2671(1)	0	0.019(2)
M2(Bi4)	2i,3, 0.333	$Bi_{0,1300}Na_{0,2033}$	0.6667	0.3333	0.3817(2)	0.0249(6)
M3(Bi5)	2i, 3, 0.333	$Bi_{0,15}Na_{0,1833}$	0.3333	0.6667	0.3790(2)	0.0212(5)
M4(Bi6)	6l, 1, 1.0	$Bi_{0,7}Na_{0,3}$	-0.0091 (1)	0.2555(1)	0.2606(1)	0.0145(2)
M5(Bi16)	2i, 3, 0.333	$Bi_{0,0333}Na_{0,3000}$	0. 3333	0.6667	0.1299(4)	0.0191(1)
M6(Bi13)	3k,*m*, 0.5	$Bi_{0,15}Na_{0,35}$	0.2521(4)	0.2579(3)	0.5	0.0470(8)
M7(Bi14)	2i, 3, 0.333	Na	0.6667	0.3333	0.1141(9)	0.019(3)
P1(P1)	6l, 1, 1.0	P	0.3795(7)	0.0272(7)	0.2504(2)	0.008(1)
P2(P3)	3j, m, 0.5	P	0.3714(8)	-0.0275(9)	0	0.011(1)
P3(P4)	3j, m, 0.5	P	0.5877(7)	0.6129(8)	0.5	0.014(1)
Cl1(Cl1)	2g,3, 0.333	Cl	0	0	0.01266(5)	0.0228(9)
Cl2(Cl3)	2g,3, 0.333	Cl	0	0	0.3737(5)	0.028(1)
O1(O2)	6l, 1, 1.0	O	0.330(2)	0.484(2)	0.2563(7)	0.030(4)
O2(O4)	3j, *m*, 0.5	O	0.465(2)	0.150(2)	0	0/014(3)
O3(O5)	3j, *m*, 0.5	O	0.849(2)	0.350(3)	0.5	0.034(5)
O4(O6)	6l, 1, 1.0	O	-0.472(2)	0.111(2)	0.2530(9)	0.032(4)
O5(O8)	6l, 1, 1.0	O	0.095(2)	0.350(2)	0.0891(8)	0.024(3)
O6(O9)	3j, *m*, 0.5	O	0.401(2)	0.524(2)	0.5	0.019(4)
O7(O11)	6l, 1, 1.0	O	-0.278(2)	0.082(2)	0.1623(8)	0.029(3)
O8(O12)	6l, 1, 1.0	O	0.901(2)	0.637(2)	0.3348(8)	0.028(3)
O9(O16)	6l, 1, 1.0	O	0.651(2)	0.726(2)	0.409(9)	0.037(4)
O10(O17)	3j, *m*, 0.5	O	0.482(2)	-0.105(3)	0	0.023(4)

*In brackets are the destinations of positions in group *P*3.

Table S3. Interatomic distances for $(Bi_{2,494}Na_{2,505})(PO_4)_3Cl$.

Bond	**Distance,** Å	**Bond**	**Distance,** Å
M1 – O17	2.13(2)	**M2** – O5x3	2.35(2)
M1 – O11x2	2.43(1)	**M2**– O6x3	2.59(2)
M1 – O8x2	2.44(1)	**M2** – O12x3	2.76(1)
Average	2.37	Average	2.57
M3-O2x3	2.44 (1)	**M5**-O2x3	2.48(2)
M3-O9x3	2,46(2)	**M5**-O17x3	2.65(2)
Average	2.45	Average	2.56
M4-O16	2.22(1)	**M6**-O9	2,. 5(2)
M4-O6	2.23(2)	**M6**-O12x2	2.51(1)
M4-O12	2.39(1)	**M6**-O16	2.62(2)
M4-O8	2.56(1)	Average	2.47
M4-O11	2.66(2)	**M7**-O4x3	2.45(1)
Average	2.41	**M7**-O6x3	2.69(2)
P1 – O11	1.49(1)	**M7**-O11x3	2.83(2)
P1 – O6	1.49(2)	Average	2.66
P1 – O12	1.52(1)	P3 – O4	1.49(2)
P1 – O2	1.53(2)	P3 – O8x2	1.57(1)
Average	1.51	P 3– O17	1.59(2)
P4– O5	1,50(2)	Average	1.55
P4– O9	1,57(2)		
P4– O16x2	1,58(1)		
Average	1.56		