Supplementary material

Temperature (K)	293
Wavelength (Å), monochromator	1.594384, Ge
2θ range, step (°)	0-160, 0.050
Total counting time (h)	4
Number of Bragg reflections	782
I / profile-dependent parameters	65 / 10
$R_P = \sum\|y_o^i - y_c^i\|/\sum y_o^i$	0.028
R_{WP} (id., weighted)	0.036
$R_{Bragg} = \sum\|I_o^i - I_c^i\|/\sum I_o^i$	0.030
$R_{exp} = ((n - p) / \sum w_i y_o^i)^{1/2}$	0.020
$R_F = \sum\|(I_o^i)^{1/2}-(I_c^i)^{1/2}\|/\sum(I_o^i)^{1/2}$	0.018
$\chi^2 = (R_{WP}/R_{exp})^2$	3.11
Space group	$R3c$ (161)
a (Å)	10.3883(1)
c (Å)	37.2221(6)
V (Å^3)	3478.78(8)
Z	6
Density (calc.)	3.15

Table S1. Data collection, refinement conditions and crystallographic data for $Ca_{9.615}Mn_{0.885}(PO_4)_7$

Atom[a]	x	y	z	B_{iso}(Å^2)	Sites	d (Å)
Ca1	-0.2727(5)	-0.1344(6)	0.1678(2)	0.45(9)	18*b*	0.07
Ca2	-0.3834(5)	-0.2101(6)	-0.0332(2)	0.12(9)	18*b*	0.36
Ca3	-0.2706(5)	-0.1245(6)	0.0615(2)	1.48(9)	18*b*	0.24
Ca4	0	0	-0.0772(8)	3.0(5)	6*a*	0.29
Mn5/Ca5	0	0	-0.2642(6)	0.8(3)	6*a*	0.08
P1	0	0	0	0.9(1)	6*a*	0
P2	-0.3117(6)	-0.1751(6)	-0.1306(2)	0.69(8)	18*b*	0.38
P3	-0.3449(6)	-0.1924(6)	-0.2329(2)	0.89(9)	18*b*	0.41
O1	-0.2629(6)	-0.1783(5)	-0.0917(2)	1.76(9)	18*b*	0.94
O2	-0.2733(5)	-0.2766(6)	-0.1522(2)	0.74(8)	18*b*	0.61
O3	-0.2365(6)	-0.0155(6)	-0.1440(2)	1.5(1)	18*b*	0.48
O4	-0.4845(5)	-0.2427(6)	-0.1342(2)	1.00(8)	18*b*	0.13
O5	-0.4194(6)	-0.1134(6)	-0.2140(2)	1.1(1)	18*b*	0.65
O6	-0.3976(5)	-0.3541(5)	-0.2209(2)	0.82(8)	18*b*	0.72
O7	-0.1788(4)	-0.1005(5)	-0.2249(2)	0.42(7)	18*b*	0.24
O8	-0.3761(4)	-0.1970(5)	-0.2735(2)	0.69(7)	18*b*	0.21
O9	0.1367(5)	-0.0070(7)	-0.0111(2)	1.45(8)	18*b*	1.36
O10	0	0	0.0427(3)	1.0(1)	6*a*	0.02

Table S2. Positional and isotropic thermal parameters of $Ca_{9.615}Mn_{0.885}(PO_4)_7$. *d* is the distance between the position of the atom in this model and its equivalent in Yashima's model [9] for undoped TCP.

Ca1-O2	2.478(8)	Ca3-O8	2.509(7)
Ca1-O3	2.94(1)	Ca3-O8	2.555(9)
Ca1-O4	2.451(7)	Ca3-O9	3.04(1)
Ca1-O4	2.466(9)	Ca3-O10	2.536(6)
Ca1-O5	2.34(1)		
Ca1-O6	2.45(1)	Ca4-O1 (3×)	2.474(8)
Ca1-O8	2.38(1)	Ca4-O9 (3×)	2.86(2)
Ca1-O9	2.479(8)		
		*M*5-O4 (3×)	2.13(1)
Ca2-O1	2.45(1)	*M*5-O7 (3×)	2.18(1)
Ca2-O2	2.39(1)		
Ca2-O3	2.43(1)	P1-O9 (3×)	1.515(7)
Ca2-O5	2.637(9)	P1-O10	1.59(1)
Ca2-O6	2.680(8)		
Ca2-O7	2.430(9)	P2-O1	1.54(1)
Ca2-O7	2.422(6)	P2-O2	1.53(1)
Ca2-O9	2.358(8)	P2-O3	1.521(8)
		P2-O4	1.573(8)
Ca3-O1	2.637(9)		
Ca3-O2	2.43(1)	P3-O5	1.55(1)
Ca3-O3	2.567(8)	P3-O6	1.550(8)
Ca3-O5	2.56(1)	P3-O7	1.526(6)
Ca3-O6	2.36(1)	P3-O8	1.54(1)

Table S3. Bond lengths (Å) in $Ca_{9.615}Mn_{0.885}(PO_4)_7$

The *M*4 site is also strongly affected by the substitution as shown in Fig. S2. In pure TCP, according to Yashima *et al*[1], this partly occupied site (43 %) is only coordinated by 3 O1 at 2.53 Å (b.v.s. = 0.65 v.u.), nearly coplanar with the cation. Next, the 3 O9 forming the face of a $P1O_4$ tetrahedron at 3.12 Å, have a nearly negligible contribution to the b.v.s. of Ca4 (0.14 v.u.), so they were not taken into account by these authors. In $Ca_{9.615}Mn_{0.885}(PO_4)_7$, the shrinkage of the $M5O_6$ octahedron results in a roughly isotropic decrease of the cell dimensions of about 0.5 %. Because the occupation of the *M*1-3 sites (in general positions) remains

unchanged, the contraction in the (001) plane affects mostly the environment of the *M*4 site, located on the same ternary axis as *M*5. So, the edge of the $O1_3$ coordination triangle shrinks from 4.36 to 4.18 Å, thus moving the cation away following the *c*-axis and bringing it closer to the $O9_3$ face (see Fig. S2). This permits a more regular distribution of the Ca4-O bonds (0.77 v.u. with the 3 O1; 0.27 v.u. with the 3 O9), thus forming a six-fold polyhedron with a higher b.v.s. (1.04 v.u.). Besides, the occupancy rate of *M*4 in Ca atoms appears ideal (50(2) %) vs 43(4) % for unsubstituted TCP. The high B_{iso} factors of the neighbor O1 and O9 atoms depict a positional disorder resulting from the incomplete occupation of the M4 site.

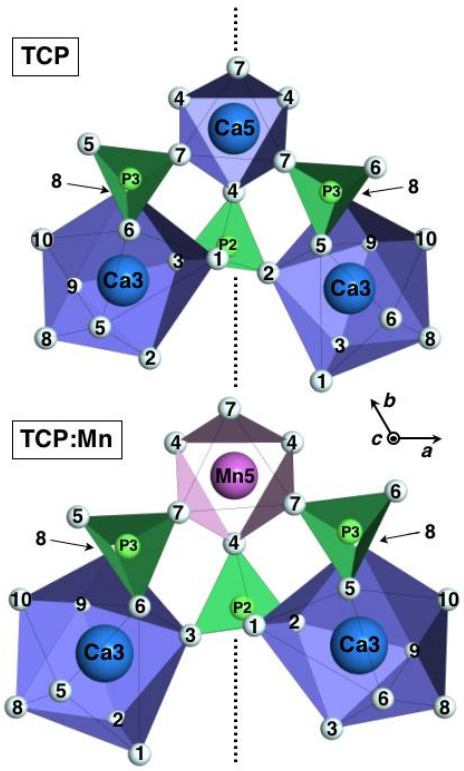

Figure S1. (001) projections of the $Ca3O_9$ and $M5O_6$ polyhedra in TCP and TCP:Mn. The *c* glide mirror (dots) matches with the *m* mirror of a pseudo *R*3*m* (*c*/2) cell. Note the correspondence between the left CaO_9 polyhedron of TCP and the right one of TCP:Mn through this *m* mirror.

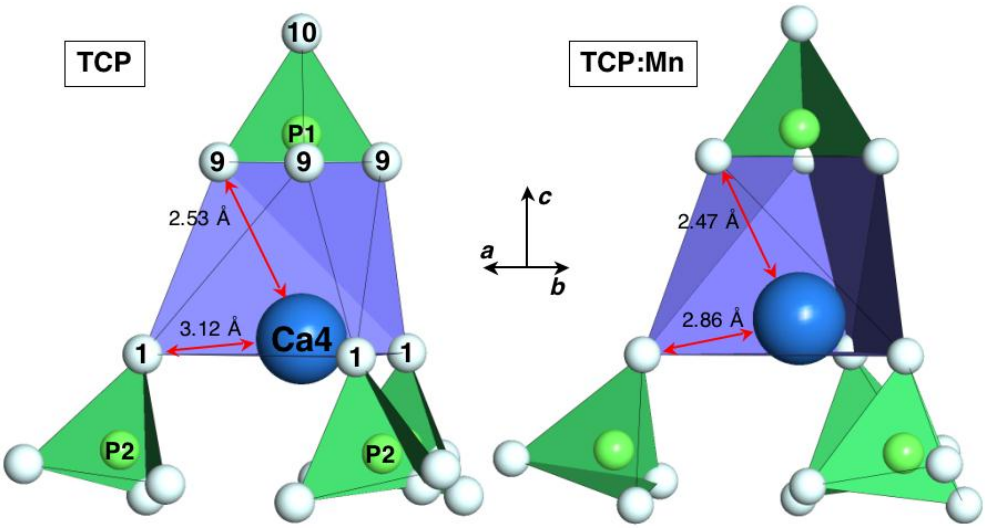

Figure S2. Environment of the Ca4 site in TCP and TCP:Mn. Note the shift of the Ca4 atom. The difference in the orientations of the $P1O_4$ tetrahedron results from the pseudo *m*-mirror.

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[1] M. Yashima, A. Sakai, T. Kamiyama and A. Hoshikawa, *J. Solid State Chem.* 2003, **175**, 272.