Supporting Information

Enhancement of the luminescent properties of a new red-emitting phosphor, $Mn_2(HPO_3)F_2$, by Zn substitution

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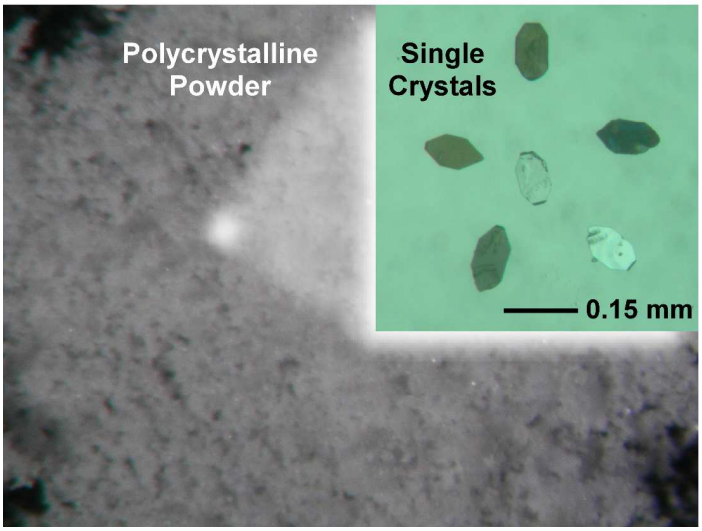


Figure S1. Polycrystalline powder of the $Mn_2(HPO_3)F_2$ phase **(1)** and single crystals of the same phase obtained as a result of the addition of $CeCl_3{\cdot}7H_2O$ to the synthesis.

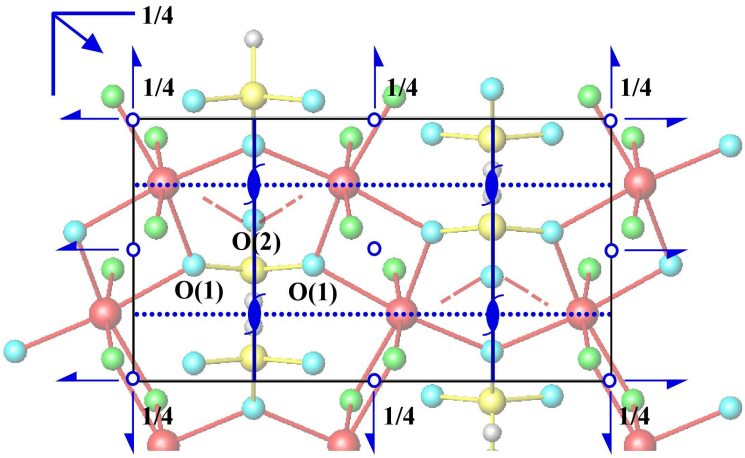
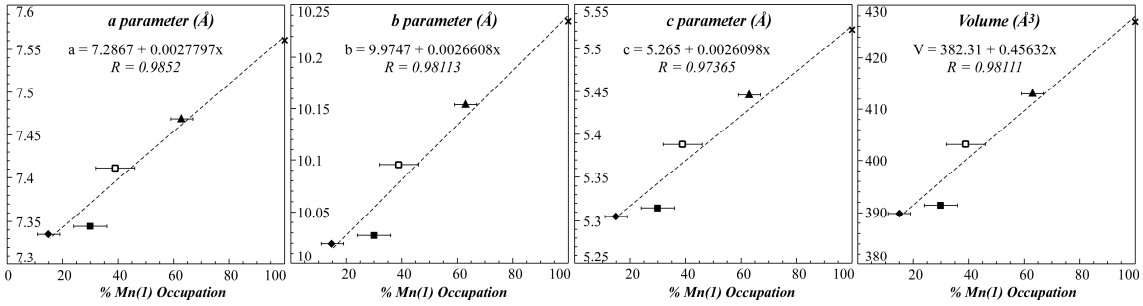
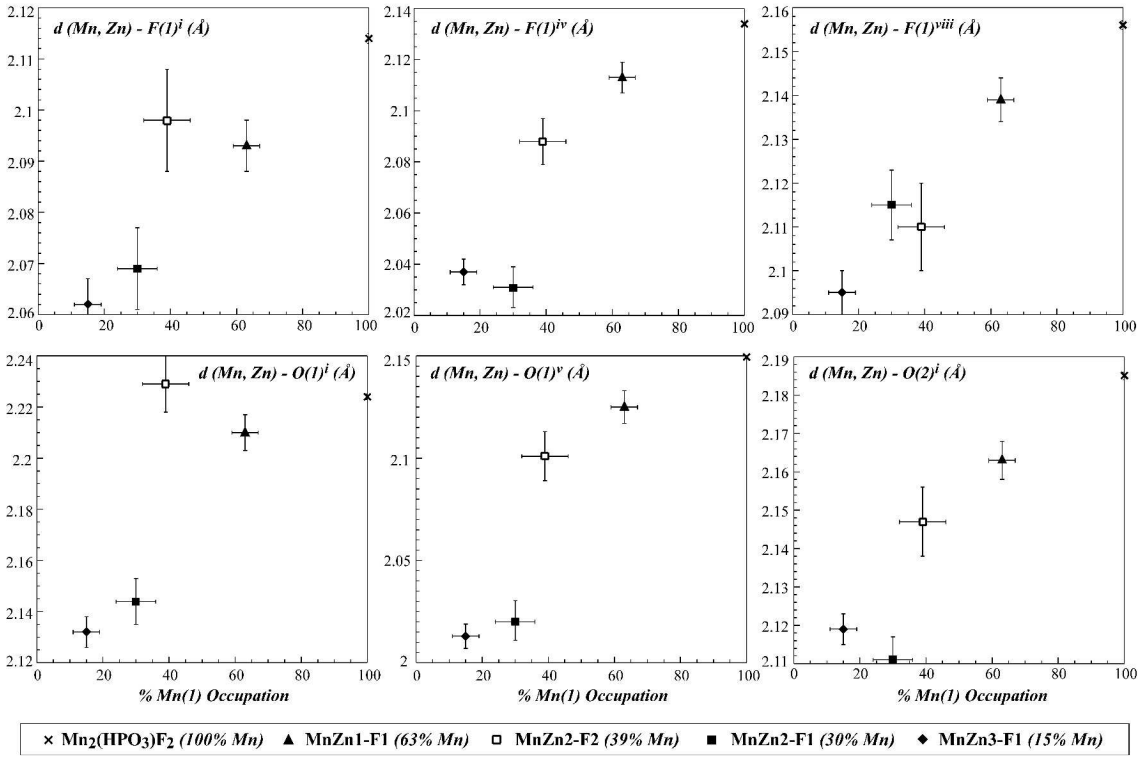


Figure S2. View of the relation of the structural subunits of the $Mn_2(HPO_3)F_2$ compound, trough the several symmetry elements characteristic of the Pnma space group, projected along the [100] direction.



(a)



(b)

Figure S3. Variation of **(a)** the unit cell parameters and **(b)** the M-O and M-F (M = Mn, Zn) distances as a function of the occupation factors of the manganese atoms for $Mn_2(HPO_3)F_2$ (**1**) and for the main solid solutions present in the *MnZn1*, *MnZn2* and *MnZn3* samples.

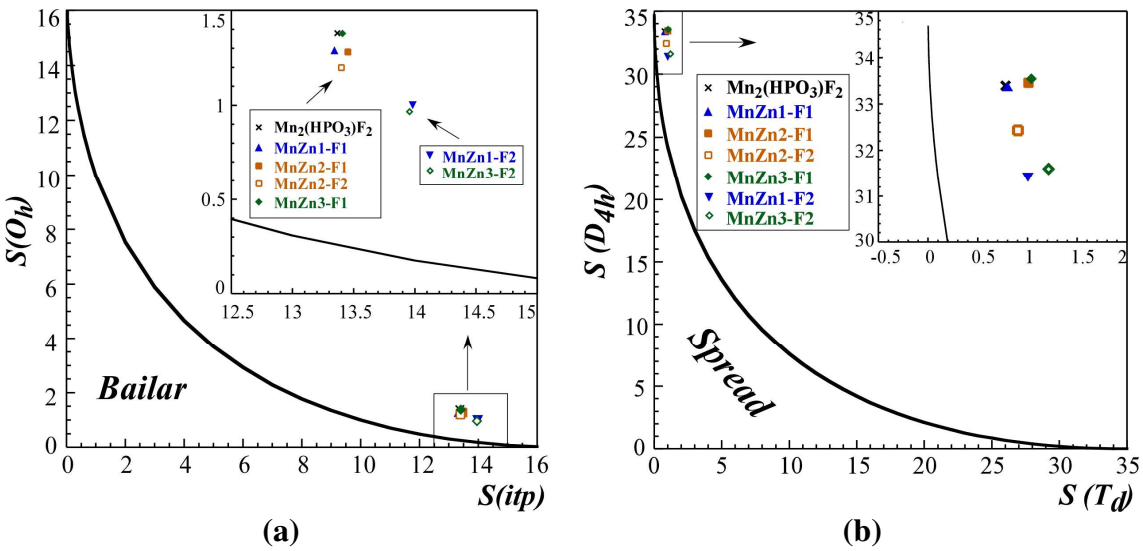


Figure S4. Distortion values of **(a)** the [(Mn,Zn)O_3F_3] octahedra and **(b)** the [HPO_3] tetrahedra belonging to $Mn_2(HPO_3)F_2$ **(1)** and to the different members of the finite solid solution of the *MnZn1*, *MnZn2*, and *MnZn3* samples.

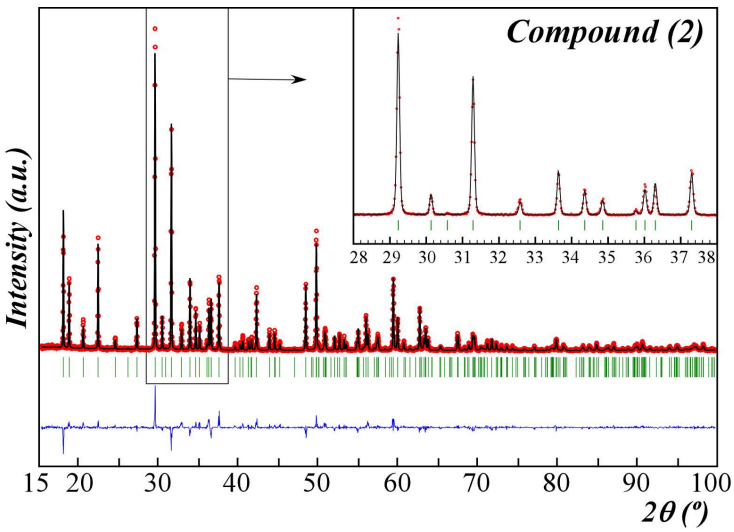


Figure S5. Observed, calculated and difference X-ray powder diffraction patterns for $Fe_2(HPO_3)F_2$ **(2)** with the structural model of $Mn_2(HPO_3)F_2$ **(1)**.

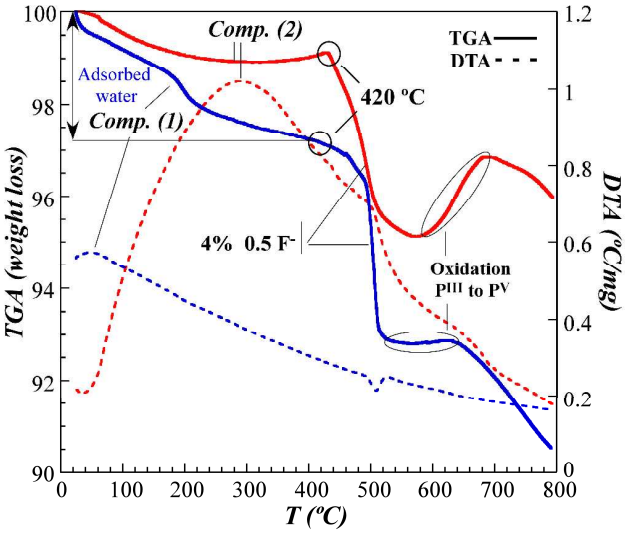


Figure S6. Thermal analysis (TGA,DTA) of $Mn_2(HPO_3)F_2$ **(1)** and $Fe_2(HPO_3)F_2$ **(2)**.

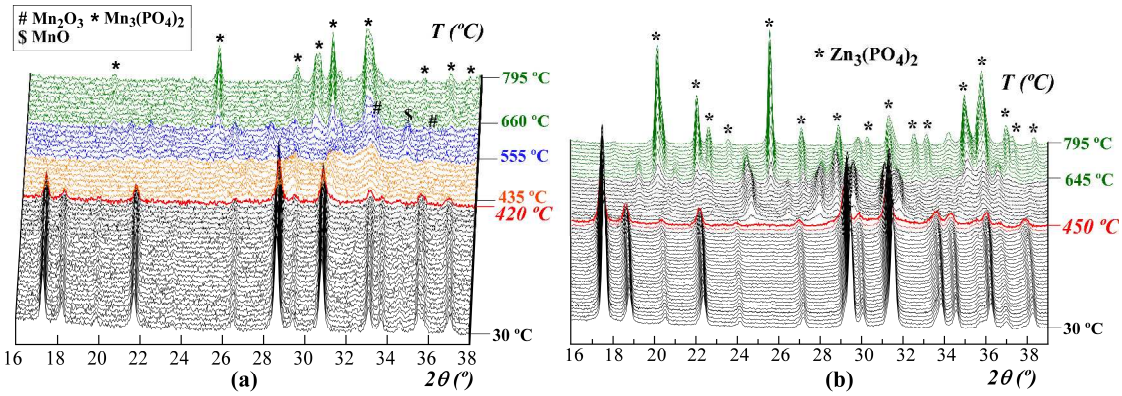


Figure S7. Thermodiffractograms of **(a)** $Mn_2(HPO_3)F_2$ **(1)** and **(b)** the *MnZn3* sample.

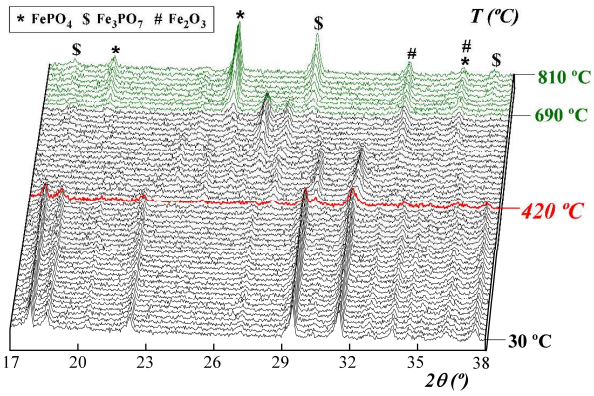


Figure S8. Thermodiffractogram of $Fe_2(HPO_3)F_2$ **(2)**.

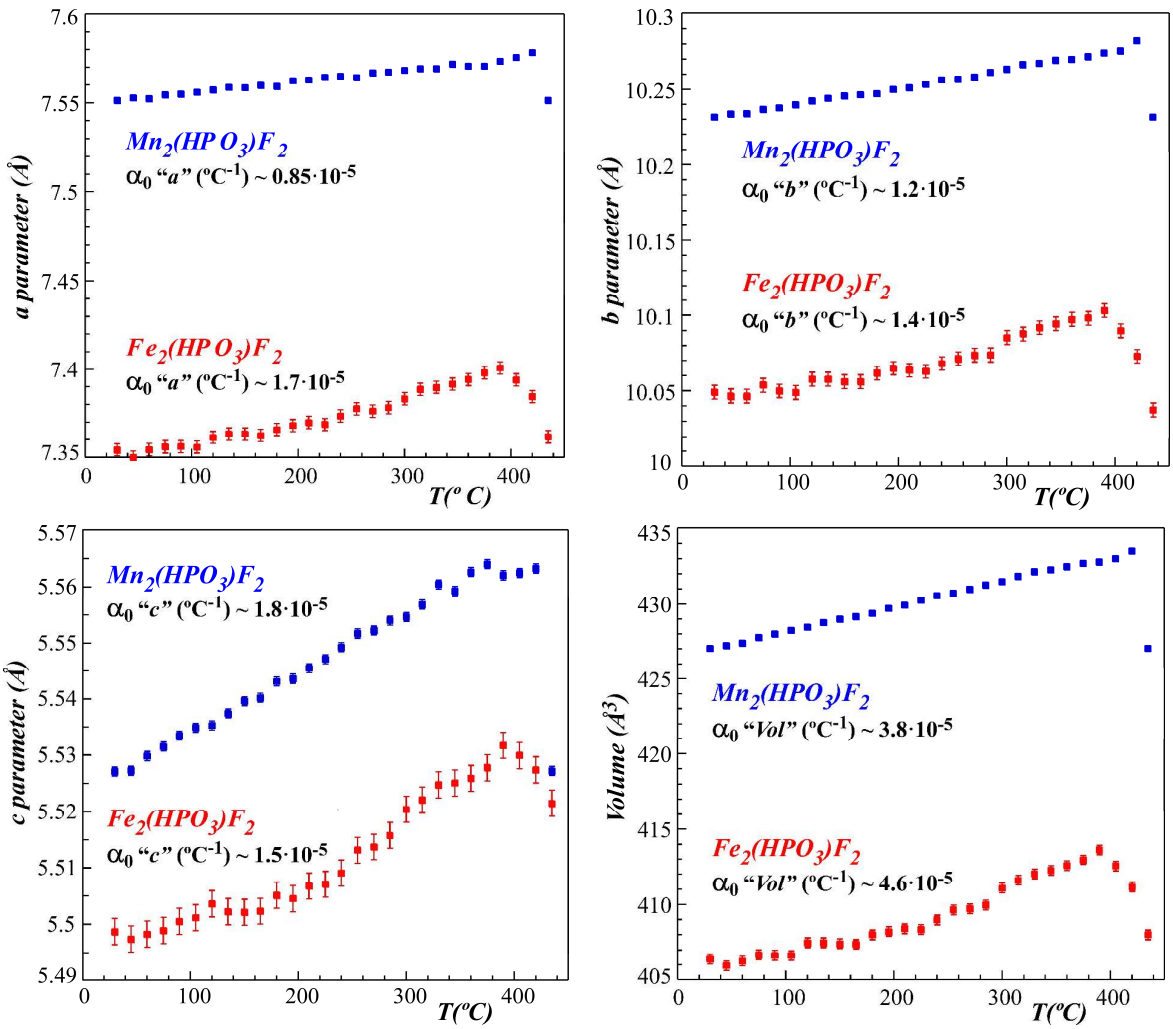


Figure S9. Thermal evolution of the parameters and volume of the unit cells for $Mn_2(HPO_3)F_2$ (**1**) and $Fe_2(HPO_3)F_2$ (**2**) in the 30 to 435 ºC temperature range.

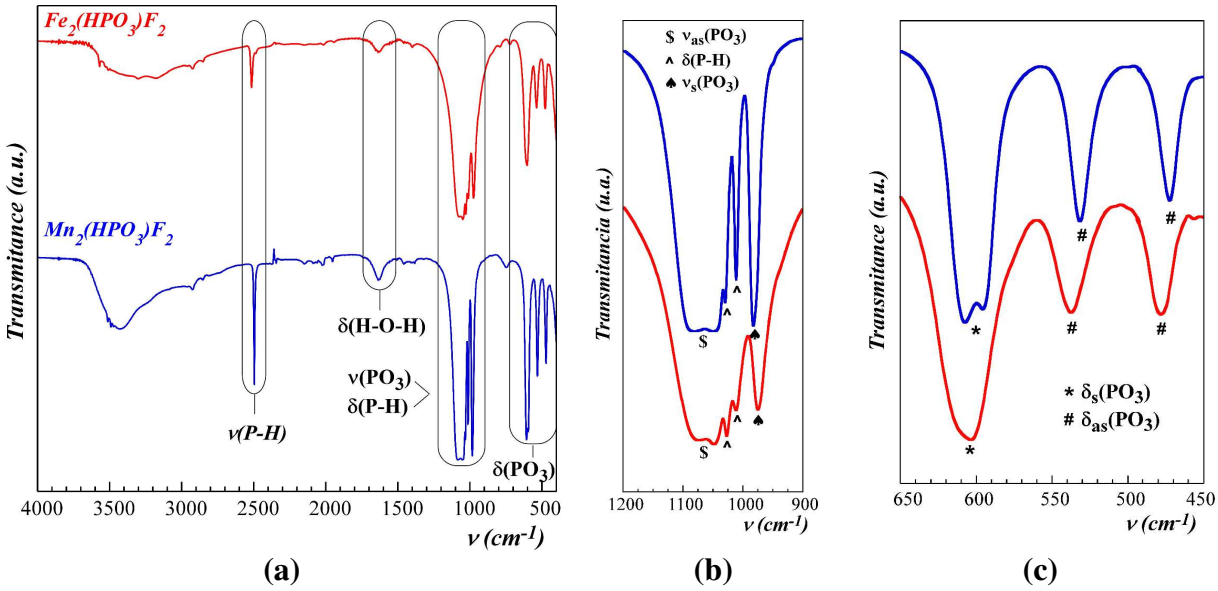


Figure S10. **(a)** Infrared spectra of the compounds **(1)** and **(2)**. Detail of the bands present in **(b)** the 900 to 1200 cm^{-1} and **(c)** the 650 to 450 cm^{-1} frequency ranges.

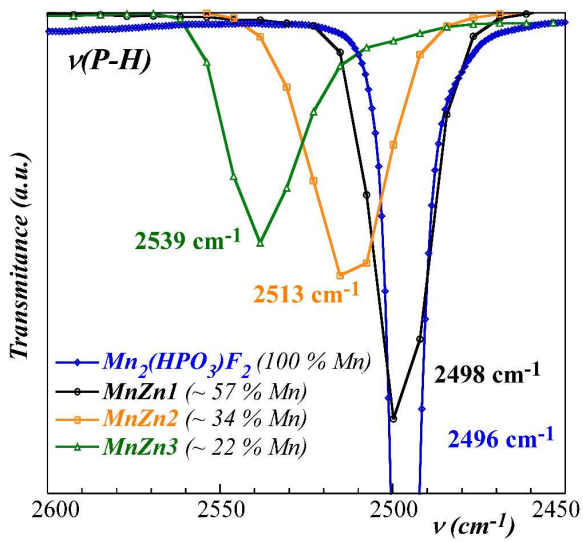


Figure S11. Wavelength shift of the bands corresponding to the stretching vibrational mode, ν(P-H), of the phosphite groups of $Mn_2(HPO_3)F_2$ **(1)** and the *MnZn1*, *MnZn2*, and *MnZn3* samples.

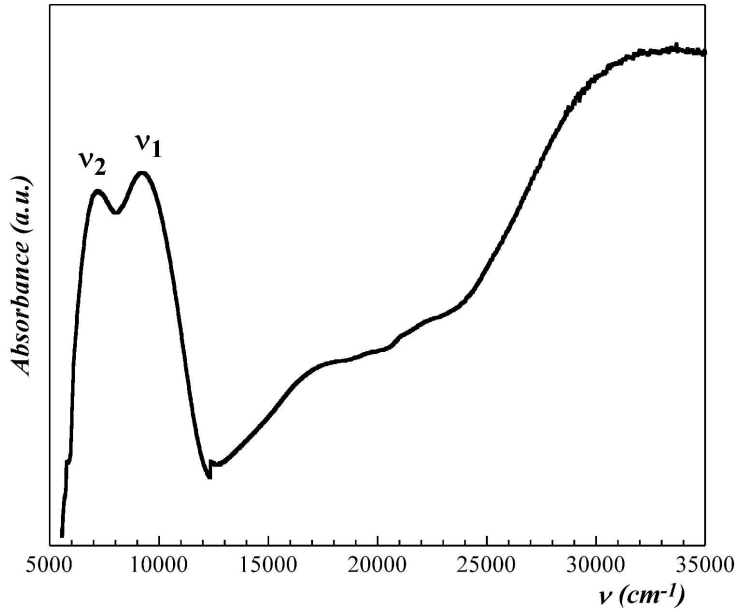


Figure S12. Diffuse reflectance spectrum of $Fe_2(HPO_3)F_2$ **(2)**.

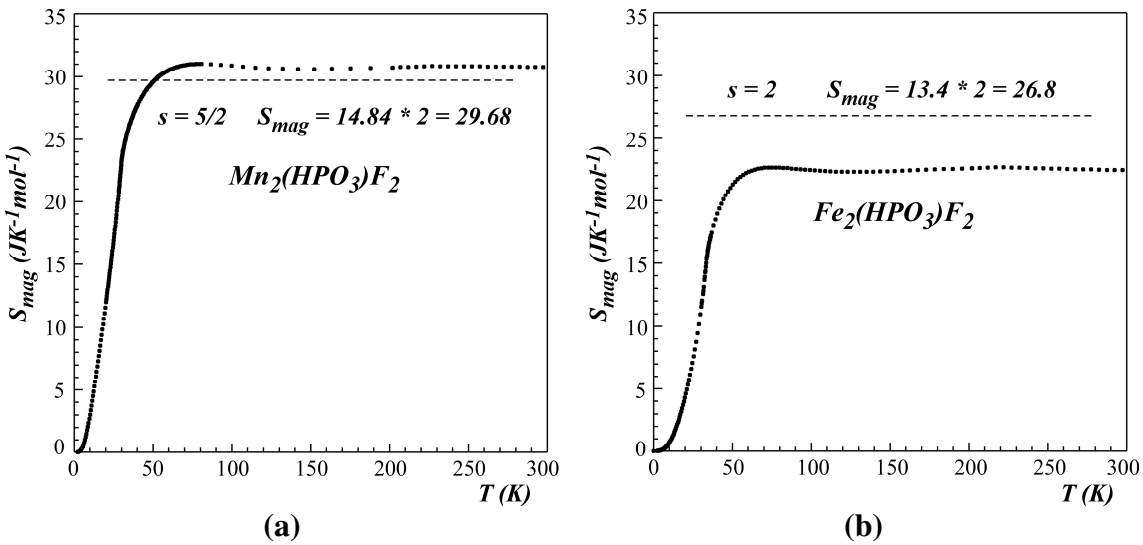


Figure S13. Magnetic entropy of **(a)** $Mn_2(HPO_3)F_2$ **(1)** and **(b)** $Fe_2(HPO_3)F_2$ **(2)** as a function of temperature. The horizontal lines show the theoretical values expected for the entropy of each system, s = 5/2. for **(1)** and s = 2 for **(2)**.

MnZn1-F1 - Rietveld Refinement

Table S1. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn1-F1*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*Occ. F.*
Mn(1)	*8d (1)*	0.0967(2)	0.4376(2)	0.2486(5)	1.23(7)	0.63(4)
Zn(1)	*8d (1)*	0.0967(2)	0.4376(2)	0.2486(5)	1.23(7)	0.37(4)
P(1)	*4c (.m.)*	0.1646(8)	0.7500	0.0853(8)	1.4(1)	0.5
F(1)	*8d (1)*	0.3437(7)	0.4542(5)	0.0698(9)	1.2(1)	1.0
O(1)	*8d (1)*	0.0512(9)	0.6278(6)	0.062(1)	1.1(1)	1.0
O(2)	*4c (.m.)*	0.181(1)	0.2500	0.398(2)	1.2(1)	0.5
H(1)	4c (.m.)	0.2322(8)	0.7500	0.2904(8)	0.5(1)	0.5

Table S2. Bond distances (Å) and angles (°) for *MnZn1-F1*.

Octahedron [(Mn,Zn)(1)O$_3$F$_3$]

Mn(1)^{i} / Zn(1)^{i}	**F(1)^{i}**	**F(1)^{iv}**	**O(1)^{v}**	**F(1)^{viii}**	**O(2)^{i}**	**O(1)^{i}**
O(1)^{i}	81.4(4)	87.7(4)	80.0(4)	90.5(4)	170.9(5)	***2.210(7)***
O(2)^{i}	89.6(4)	94.9(3)	100.0(5)	98.6(5)	***2.163(5)***	
F(1)^{viii}	170.9(4)	76.3(3)	86.2(4)	***2.139(5)***		
O(1)^{v}	96.5(4)	158.5(5)	***2.125(8)***			
F(1)^{iv}	99.1(4)	***2.113(6)***				
F(1)^{i}	***2.093(5)***					

Tetrahedron [HP(1)O$_3$]

P(1)^{i}	**O(1)^{i}**	**O(1)^{vii}**	**O(2)^{iv}**	**H(1)^{i}**
H(1)^{i}	108.0(7)	108.0(7)	107.0(9)	***1.226(7)***
O(2)^{iv}	111.4(9)	111.4(9)	***1.55(1)***	
O(1)^{vii}	110.8(7)	***1.508(7)***		
O(1)^{i}	***1.508(7)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

MnZn1-F2 - Rietveld Refinement

Table S3. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn1-F2*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*F. Oc.*
Mn(1)	*8d (1)*	0.0960(7)	0.4374(6)	0.248(2)	3.8(4)	0.29(5)
Zn(1)	*8d (1)*	0.0960(7)	0.4374(6)	0.248(2)	3.8(4)	0.71(5)
P(1)	*4c (.m.)*	0.176(2)	0.7500	0.086(2)	3.8(6)	0.5
F(1)	*8d (1)*	0.345(3)	0.454(2)	0.067(3)	3.6(6)	1.0
O(1)	*8d (1)*	0.038(3)	0.632(2)	0.066(5)	3.5(6)	1.0
O(2)	*4c (.m.)*	0.181(5)	0.2500	0.393(5)	3.6(6)	0.5
H(1)	*4c (.m.)*	0.244(2)	0.7500	0.291(2)	3.0(6)	0.5

Table S4. Bond distances (Å) and angles (°) for *MnZn1-F2*.

Octahedron [(Mn,Zn)(1)O_3F_3]

Mn(1)^{i} / Zn(1)^{i}	**F(1)^{iv}**	**O(1)^{v}**	**F(1)^{i}**	**F(1)^{viii}**	**O(2)^{i}**	**O(1)^{i}**
O(1)^{i}	86(1)	81(1)	84(1)	88(1)	173(2)	***2.24(2)***
O(2)^{i}	96(1)	98(2)	89(1)	99(2)	***2.14(2)***	
F(1)^{viii}	76(1)	89(2)	171(2)	***2.12(2)***		
F(1)^{i}	99(1)	94(2)	***2.10(2)***			
O(1)^{v}	161(2)	***2.09(3)***				
F(1)^{iv}	***2.09(2)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(2)^{iv}**	**O(1)^{i}**	**O(1)^{vii}**	**H(1)^{i}**
H(1)^{i}	110(3)	109(2)	109(2)	***1.22(2)***
O(1)^{vii}	115(3)	98(2)	***1.58(2)***	
O(1)^{i}	115(3)	***1.58(2)***		
O(2)^{iv}	***1.49(4)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

MnZn2-F1 - Rietveld Refinement

Table S5. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn2-F1*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*F. Oc.*
Mn(1)	*8d (1)*	0.0949(3)	0.4382(2)	0.2482(6)	2.41(6)	0.30(6)
Zn(1)	*8d (1)*	0.0949(3)	0.4382(2)	0.2482(6)	2.41(6)	0.70(6)
P(1)	*4c (.m.)*	0.164(1)	0.7500	0.087(1)	3.7(2)	0.5
F(1)	*8d (1)*	0.342(1)	0.4588(7)	0.065(3)	2.7(2)	1.0
O(1)	*8d (1)*	0.047(1)	0.6232(8)	0.057(2)	2.6(2)	1.0
O(2)	*4c (.m.)*	0.174(2)	0.2500	0.389(2)	2.8(2)	0.5
H(1)	*4c (.m.)*	0.232(1)	0.7500	0.292(1)	1.0(2)	0.5

Table S6. Bond distances (Å) and angles (°) for *MnZn2-F1*.

Octahedron [(Mn,Zn)(1)O_3F_3]

Mn(1)^{i} / Zn(1)^{i}	**O(1)^{v}**	**F(1)^{iv}**	**F(1)^{i}**	**O(2)^{i}**	**F(1)^{viii}**	**O(1)^{i}**
O(1)^{i}	78.4(5)	89.5(6)	80.6(5)	170.6(6)	89.6(5)	***2.144(9)***
F(1)^{viii}	87.4(6)	76.2(5)	168.7(6)	99.3(6)	***2.115(8)***	
O(2)^{i}	98.8(7)	95.6(4)	90.9(5)	***2.111(6)***		
F(1)^{i}	96.0(6)	98.0(5)	***2.069(8)***			
F(1)^{iv}	159.7(7)	***2.031(8)***				
O(1)^{v}	***2.02(1)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(1)^{i}**	**O(1)^{vii}**	**O(2)^{iv}**	**H(1)^{i}**
H(1)^{i}	108.8(9)	108.8(9)	106.9(11)	***1.198(9)***
O(2)^{iv}	110.6(11)	110.6(11)	***1.589(15)***	
O(1)^{vii}	110.9(9)	***1.544(10)***		
O(1)^{i}	***1.544(10)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

MnZn2-F2 - Rietveld Refinement

Table S7. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn2-F2*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*F. Oc.*
Mn(1)	*8d (1)*	0.0972(4)	0.4378(3)	0.2457(7)	2.82(8)	0.39(7)
Zn(1)	*8d (1)*	0.0972(4)	0.4378(3)	0.2457(7)	2.82(8)	0.61(7)
P(1)	*4c (.m.)*	0.166(1)	0.7500	0.085(1)	2.9(2)	0.5
F(1)	*8d (1)*	0.348(1)	0.4546(9)	0.062(2)	2.6(2)	1.0
O(1)	*8d (1)*	0.050(2)	0.632(1)	0.061(2)	2.6(2)	1.0
O(2)	*4c (.m.)*	0.173(3)	0.2500	0.401(3)	2.7(2)	0.5
H(1)	*4c (.m.)*	0.233(1)	0.7500	0.290(1)	2.2(2)	0.5

Table S8. Bond distances (Å) and angles (°) for *MnZn2-F2*.

Octahedron [(Mn,Zn)(1)O_3F_3]

Mn(1)^{i} / Zn(1)^{i}	**F(1)^{iv}**	**F(1)^{i}**	**O(1)^{v}**	**F(1)^{viii}**	**O(2)^{i}**	**O(1)^{i}**
O(1)^{i}	86.8(6)	82.2(7)	82.1(7)	90.2(7)	173.2(8)	***2.229(11)***
O(2)^{i}	94.8(5)	91.0(7)	98.3(9)	96.6(9)	***2.147(9)***	
F(1)^{viii}	74.5(6)	170.7(8)	87.0(7)	***2.110(10)***		
O(1)^{v}	158.4(8)	97.3(8)	***2.101(12)***			
F(1)^{i}	99.5(6)	***2.098(10)***				
F(1)^{iv}	***2.088(9)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(1)^{i}**	**O(1)^{vii}**	**O(2)^{iv}**	**H(1)^{i}**
H(1)^{i}	109(1)	109(1)	105(2)	***1.21(1)***
O(2)^{iv}	113(2)	113(2)	***1.55(2)***	
O(1)^{vii}	108(1)	***1.47(1)***		
O(1)^{i}	***1.47(1)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

MnZn3-F1 - Rietveld Refinement

Table S9. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn3-F1*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*F. Oc.*
Mn(1)	*8d (1)*	0.0963(2)	0.4382(1)	0.2493(4)	3.67(4)	0.15(4)
Zn(1)	*8d (1)*	0.0963(2)	0.4382(1)	0.2493(4)	3.67(4)	0.85(4)
P(1)	*4c (.m.)*	0.1623(7)	0.7500	0.0874(8)	4.2(1)	0.5
F(1)	*8d (1)*	0.3440(7)	0.4584(4)	0.0695(9)	3.8(1)	1.0
O(1)	*8d (1)*	0.0439(8)	0.6210(5)	0.057(1)	3.8(1)	1.0
O(2)	*4c (.m.)*	0.178(1)	0.2500	0.393(2)	3.8(1)	0.5
H(1)	*4c (.m.)*	0.2299(7)	0.7500	0.2925(8)	3.8(1)	0.5

Table S10. Bond distances (Å) and angles (°) for *MnZn3-F1*.

Octahedron [(Mn,Zn)(1)O_3F_3]

Mn(1)^{i} / Zn(1)^{i}	**O(1)^{v}**	**F(1)^{iv}**	**F(1)^{i}**	**F(1)^{viii}**	**O(2)^{i}**	**O(1)^{i}**
O(1)^{i}	77.0(3)	90.0(4)	81.6(3)	88.7(4)	170.8(4)	***2.132(6)***
O(2)^{i}	99.9(5)	95.3(3)	90.3(3)	99.8(4)	***2.119(4)***	
F(1)^{viii}	87.0(4)	76.0(3)	168.8(4)	***2.095(5)***		
F(1)^{i}	96.1(4)	98.4(4)	***2.062(5)***			
F(1)^{iv}	158.9(5)	***2.037(5)***				
O(1)^{v}	***2.013(6)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(2)^{iv}**	**O(1)^{i}**	**O(1)^{vii}**	**H(1)^{i}**
H(1)^{i}	106.9(8)	108.9(6)	108.9(6)	***1.196(6)***
O(1)^{vii}	110.4(7)	111.3(5)	***1.565(6)***	
O(1)^{i}	110.4(7)	***1.565(6)***		
O(2)^{iv}	***1.562(10)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

MnZn3-F2 - Rietveld Refinement

Table S11. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for *MnZn3-F2*.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*F. Oc.*
Mn(1)	*8d (1)*	0.0954(5)	0.4371(4)	0.255(1)	1.4(1)	0.50(9)
Zn(1)	*8d (1)*	0.0954(5)	0.4371(4)	0.255(1)	1.4(1)	0.50(9)
P(1)	*4c (.m.)*	0.162(1)	0.7500	0.090(2)	2.1(3)	0.5
F(1)	*8d (1)*	0.333(2)	0.451(1)	0.080(2)	1.1(3)	1.0
O(1)	*8d (1)*	0.036(2)	0.622(1)	0.051(3)	1.1(3)	1.0
O(2)	*4c (.m.)*	0.172(2)	0.2500	0.420(3)	1.1(3)	0.5
H(1)	*4c (.m.)*	0.230(1)	0.7500	0.295(2)	1.1(3)	0.5

Table S12. Bond distances (Å) and angles (°) for *MnZn3-F2*.

Octahedron [(Mn,Zn)(1)O_3F_3]

Mn(1)^{i} / Zn(1)^{i}	**F(1)^{i}**	**O(1)^{v}**	**F(1)^{viii}**	**F(1)^{iv}**	**O(2)^{i}**	**O(1)^{i}**
O(1)^{i}	83.4(9)	76.5(9)	88.3(9)	89.9(9)	173.8(9)	***2.22(2)***
O(2)^{i}	91.2(8)	101(1)	97.2(8)	93.7(7)	***2.155(9)***	
F(1)^{iv}	97.4(8)	161(1)	81.6(8)	***2.14(1)***		
F(1)^{viii}	172(1)	85.3(9)	***2.13(1)***			
O(1)^{v}	94(1)	***2.00(2)***				
F(1)^{i}	***1.99(1)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(2)^{iv}**	**O(1)^{i}**	**O(1)^{vii}**	**H(1)^{i}**
H(1)^{i}	102(2)	111(1)	111(1)	***1.21(1)***
O(1)^{vii}	113(2)	106(1)	***1.58(2)***	
O(1)^{i}	113(2)	***1.58(2)***		
O(2)^{iv}	***1.52(2)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

Table S13. Distortion values for $[M(1)O_3F_3]$ (M = Mn, Zn) and $[HP(1)O_3]$ coordination polyhedra for **(1)** and the phases present in the *MnZn1*, *MnZn2* and *MnZn3* samples.

	$[M(1)O_3F_3]$		**$[HP(1)O_3]$**	
	$S(O_h)$	**S(itp)**	**$S(T_d)$**	**$S(D_{4h})$**
$Mn_2(HPO_3)F_2$ (1)	1.380	13.373	0.780	33.394
MnZn1-F1	1.287	13.343	0.798	33.372
MnZn1-F2	1.003	13.981	1.003	31.418
MnZn2-F1	1.281	13.452	1.010	33.461
MnZn2-F2	1.199	13.399	0.904	32.435
MnZn3-F1	1.379	13.410	1.039	33.544
MnZn3-F2	0.967	13.958	1.213	31.600

$Fe_2(HPO_3)F_2$ (2) – Rietveld Refinement

Table S14. Crystallographic parameters and characteristics of the Rietveld refinement for **(2)**.

Phase	**Compound (2)**
Formula	$Fe_2(HPO_3)F_2$
Molecular weight ($gmol^{-1}$)	229.667
Crystal system	Orthorhombic
Space group (Nº 62)	Pnma
ATZ	918.668
a, Å	7.3443(1)
b, Å	10.0330(1)
c, Å	5.49166(8)
V, $Å^3$	404.66(1)
Z	4
Independent Reflections	237
Structural Parameters	19
Profile Parameters	35
R_{Bragg}	12.6
R_f	7.62
R_p	15.9
R_{wp}	20.9
R_{exp}	16.09
χ^2	1.69

Table S15. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for **(2)**.

Atoms	*Wyckoff*	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*Occ. F.*
Fe(1)	*8d (1)*	0.0974(2)	0.4390(2)	0.2483(5)	1.62(6)	1.0
P(1)	*4c (.m.)*	0.1637(7)	0.7500(0)	0.0833(9)	1.8(1)	0.5
F(1)	*8d (1)*	0.3451(8)	0.4509(6)	0.082(1)	2.4(2)	1.0
O(1)	*8d (1)*	0.052(1)	0.6280(6)	0.068(1)	1.4(2)	1.0
O(2)	*4c (.m.)*	0.177(1)	0.2500(1)	0.390(2)	0.9(2)	0.5
H(1)	*4c (.m.)*	0.2313(7)	0.7500(0)	0.2885(9)	1.7	0.5

Table S16.- Bond distances (Å) and angles (°) for **(2)**.

Octahedron [Fe(1)O_3F_3]

Fe(1)^{i}	**F(1)^{i}**	**F(1)^{viii}**	**O(2)^{i}**	**O(1)^{v}**	**O(1)^{i}**	**F(1)^{iv}**
F(1)^{iv}	100.0(4)	76.5(4)	95.2(3)	158.6(6)	88.3(4)	***2.181(7)***
O(1)^{i}	83.2(4)	90.9(4)	171.3(4)	80.0(4)	***2.167(7)***	
O(1)^{v}	96.3(5)	85.8(4)	99.0(5)	***2.158(8)***		
O(2)^{i}	88.3(4)	97.6(4)	***2.132(4)***			
F(1)^{viii}	173.3(5)	***2.078(6)***				
F(1)^{i}	***2.039(6)***					

Tetrahedron [HP(1)O_3]

P(1)^{i}	**O(1)^{i}**	**O(1)^{vii}**	**O(2)^{iv}**	**H(1)^{i}**
H(1)^{i}	106.1(7)	106.1(7)	108.5(8)	***1.231(7)***
O(2)^{iv}	111.9(8)	111.9(8)	***1.58(1)***	
O(1)^{vii}	111.8(7)	***1.478(7)***		
O(1)^{i}	***1.478(7)***			

Symmetry codes: *i* = x, y, z; *ii* = x+1/2, -y+1/2, -z+1/2; *iii* = -x, y+1/2, -z; *iv* = -x+1/2, -y, z+1/2; *v* = -x, -y, -z; *vi* = -x+1/2, y+1/2, z+1/2; *vii* = x, -y+1/2, z; *viii* = x+1/2, y, -z+1/2.

Table S17. Thermal expansion coefficients of the parameters and volume of the unit cells for **(1)** and **(2)**.

	$Mn_2(HPO_3)F_2$ *(1)*	$Fe_2(HPO_3)F_2$ *(2)*
α_o *a* ($^oC^{-1}$)	$0.85 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$
α_o *b* ($^oC^{-1}$)	$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$
α_o *c* ($^oC^{-1}$)	$1.8 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$
α_o *V* ($^oC^{-1}$)	$3.8 \cdot 10^{-5}$	$4.6 \cdot 10^{-5}$

Table S18. Assignment of the infrared spectra bands of the compounds **(1)** and **(2).**

Band (cm^{-1})	$Mn_2(HPO_3)F_2$ *(1)*	$Fe_2(HPO_3)F_2$ *(2)*
ν*(P-H)*	2495 *in*	2515 *wn*
$\nu_{as}(PO_3)$	1070 *ib*	1060 *ib*
δ*(P-H)*	1030, 1015 *in*	1030, 1015 *in*
$\nu_s(PO_3)$	980 *in*	970 *mn*
$\delta_s(PO_3)$	600 *in*	605 *in*
$\delta_{as}(PO_3)$	530, 470 *mn*	535, 480 *mn*

The bands are classified by : *i* = intense, *m* = medium, *w* = weak, *n* = narrow, *b* = broad, ν = stretching, δ = deformation, *s* = symmetrical and *as* = asymmetrical.